Photothermal Spectroscopy
Lecture 2 - Applications

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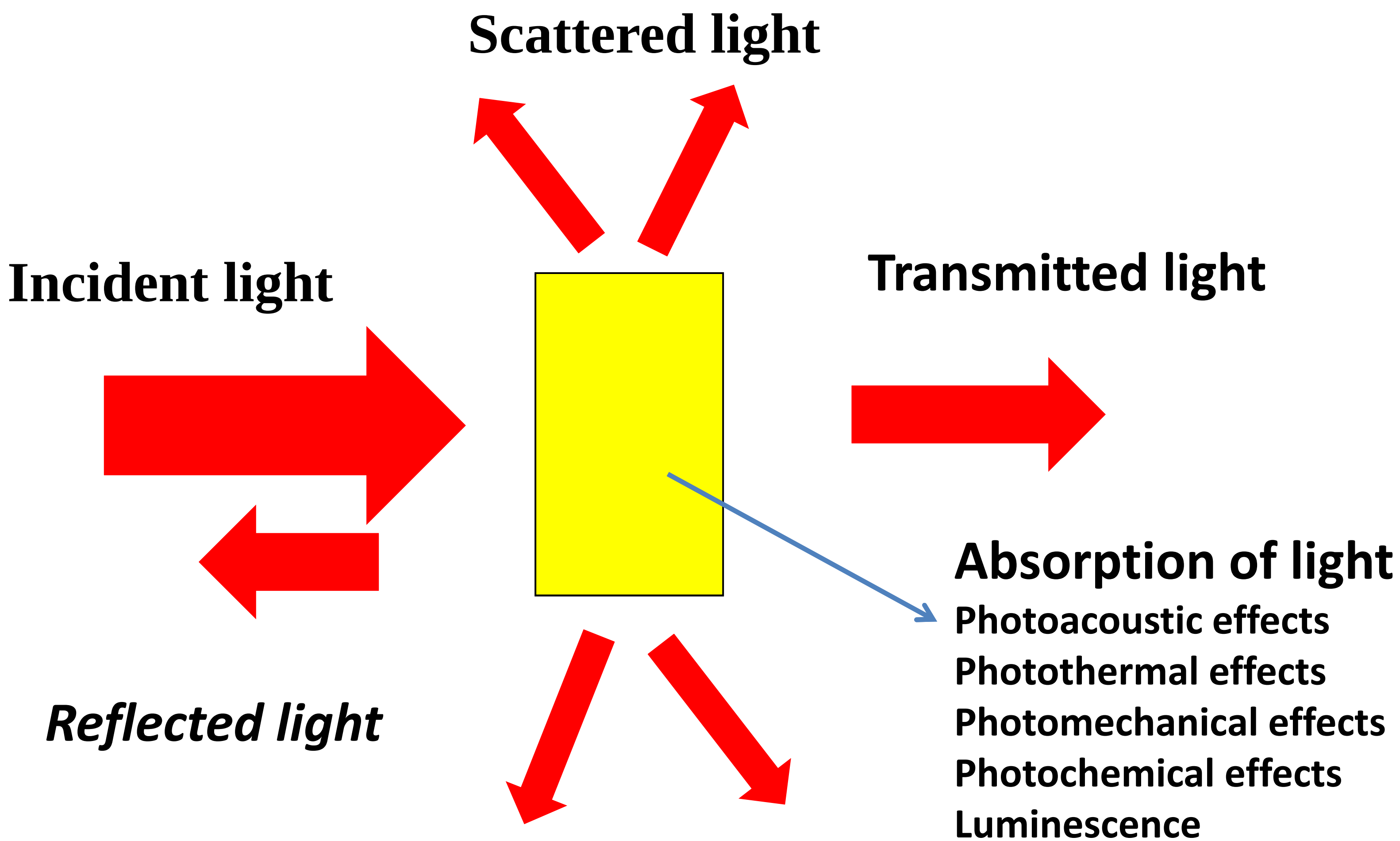
Outlook

1. Optical characterization of matter.
2. The place of photothermal spectroscopy
3. Achromatic character of the mode-mismatched configuration.
4. NIR Photothermal spectroscopy
5. Photothermal-absorbance-fluorescence spectrophotometer.
6. Photothermal spectroscopy of fluorescence and scattering samples.
7. Perspectives.

Material samples exhibit generally more than one type of effect upon interaction with light



From the energy conservation law we obtain

$$P_o(\lambda) = P_T(\lambda) + P_F(\lambda) + P_{Th}(\lambda) + P_s(\lambda) + P_R(\lambda)$$

$P_o(\lambda)$ **Incident power**

$P_T(\lambda)$ **Transmitted power**

$P_F(\lambda)$ **Power used for fluorescence**

$P_{Th}(\lambda)$ **Power degraded into heat**

$P_s(\lambda)$ **Scattered power**

$P_R(\lambda)$ **Reflected power**

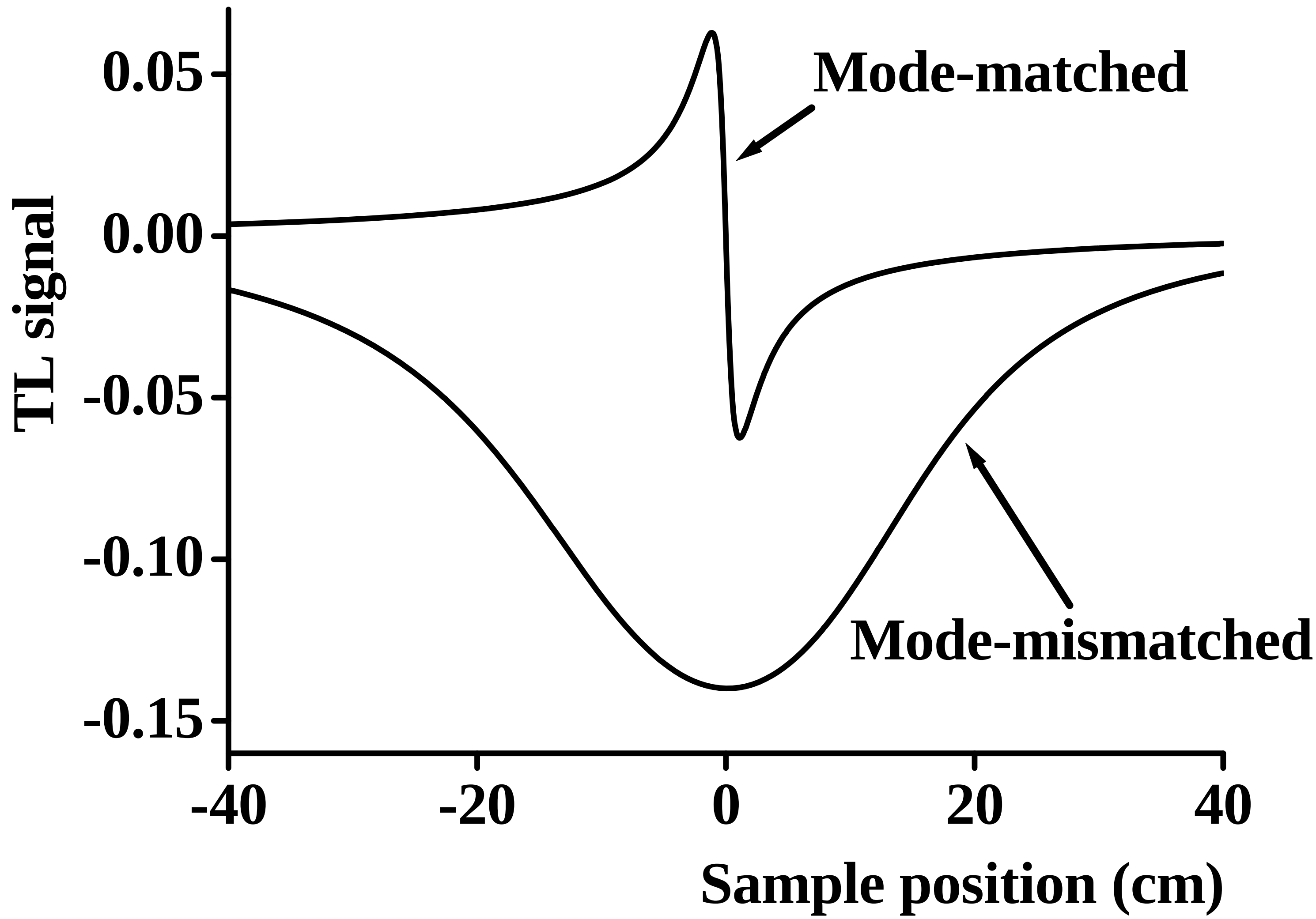
$$T(\lambda) = \frac{P_T(\lambda)}{P_o(\lambda)}$$ Transmittance

$$A(\lambda) = -\log T(\lambda)$$ Absorbance

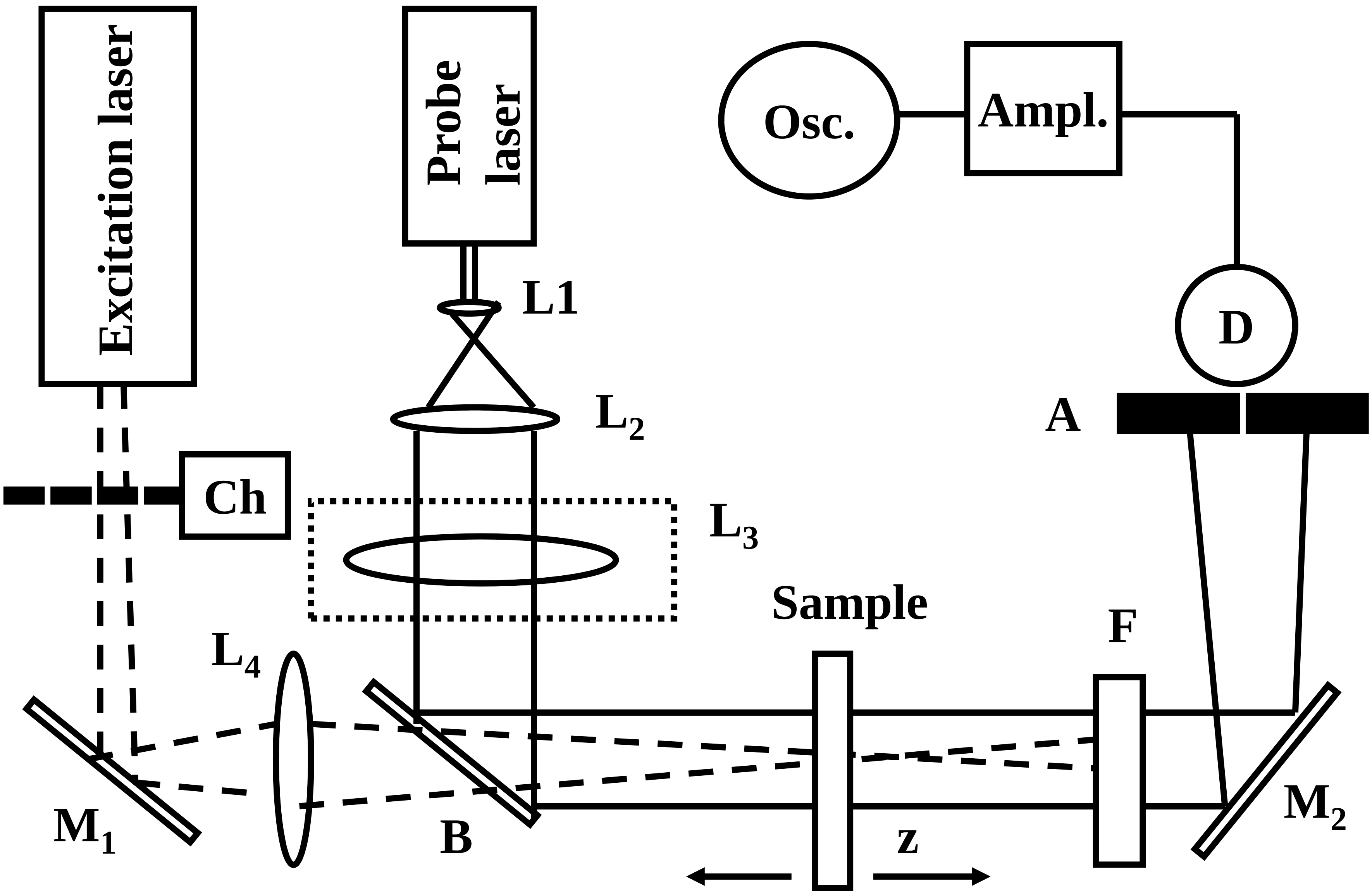
$$R(\lambda) = \frac{P_R(\lambda)}{P_o(\lambda)}$$ Reflectance

$$F(\lambda) = \frac{P_F(\lambda)}{P_o(\lambda)}$$ Fluorescence excitation spectrum

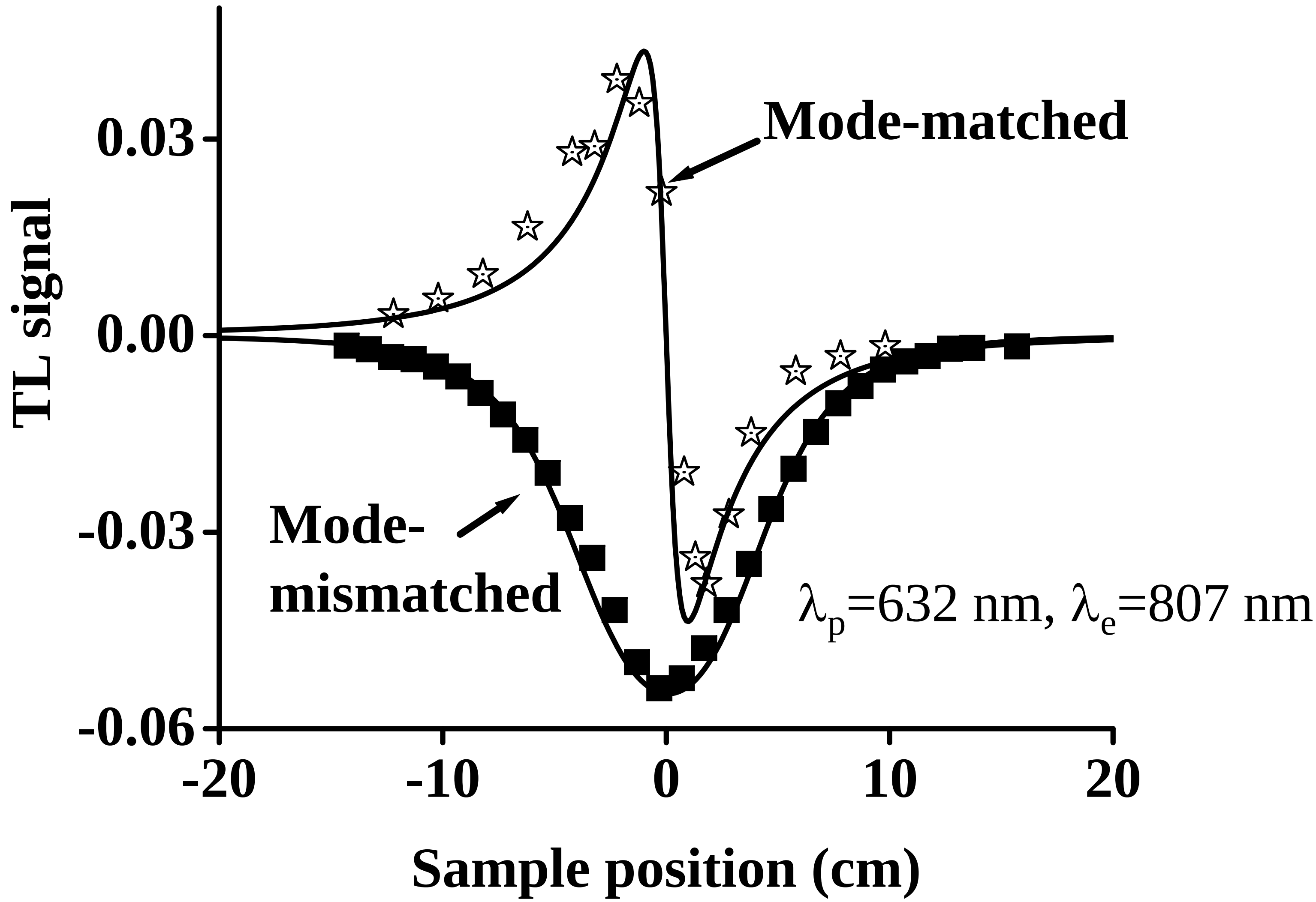
$$PT(\lambda) = \frac{P_{Th}(\lambda)}{P_o(\lambda)}$$ Photothermal spectrum



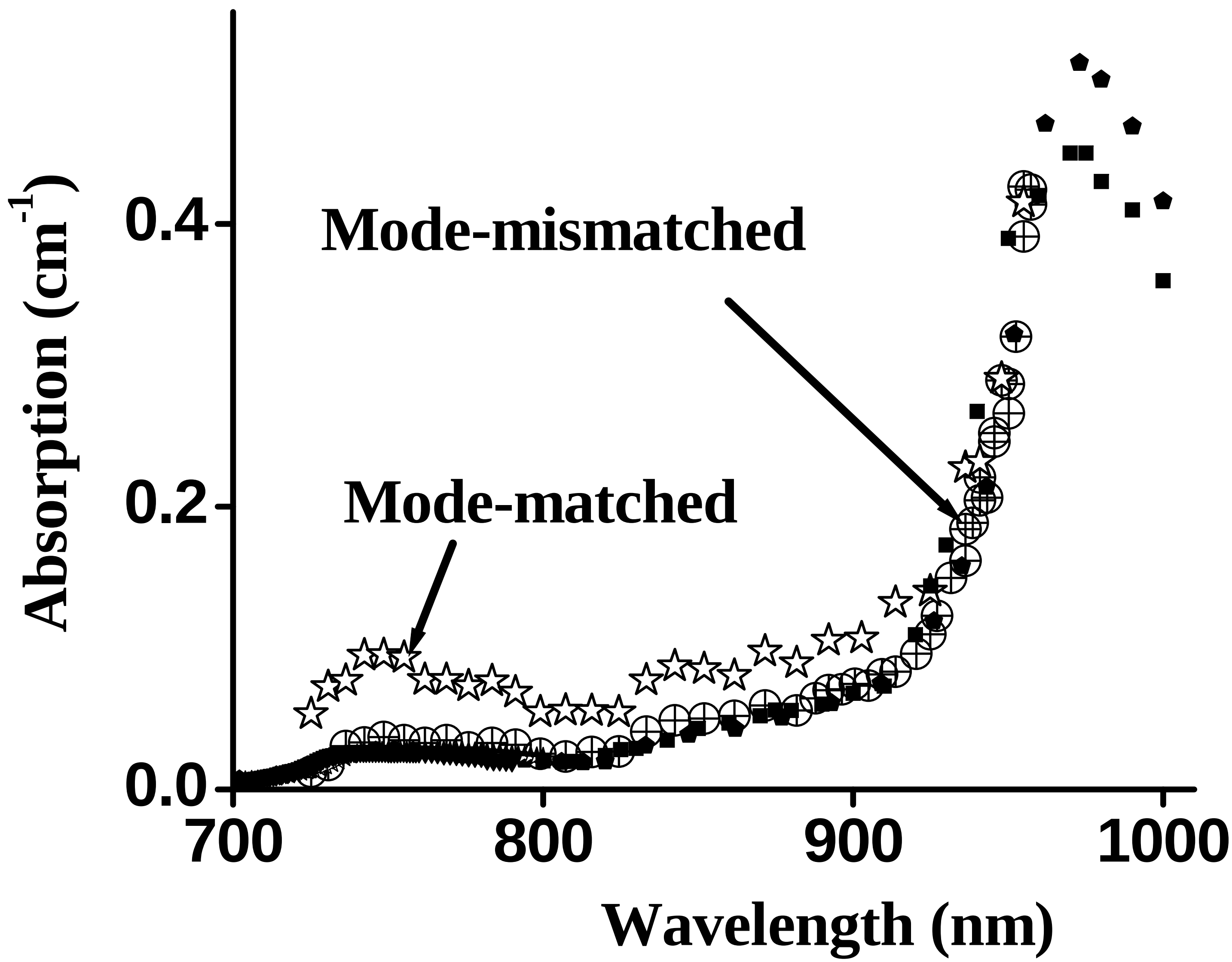
Φ_o=-0.1, λ_p=632 nm, λ_e=750 nm, L=200 cm, D=0.001491 cm^2/s, t=10 s, z_p=0.2 cm for mode-matched scheme and z_p=2000 cm for mode-mismatched scheme.



Marcano O. A. and N. Melikechi, App. Spectros. **61**, 659-664 (2007).



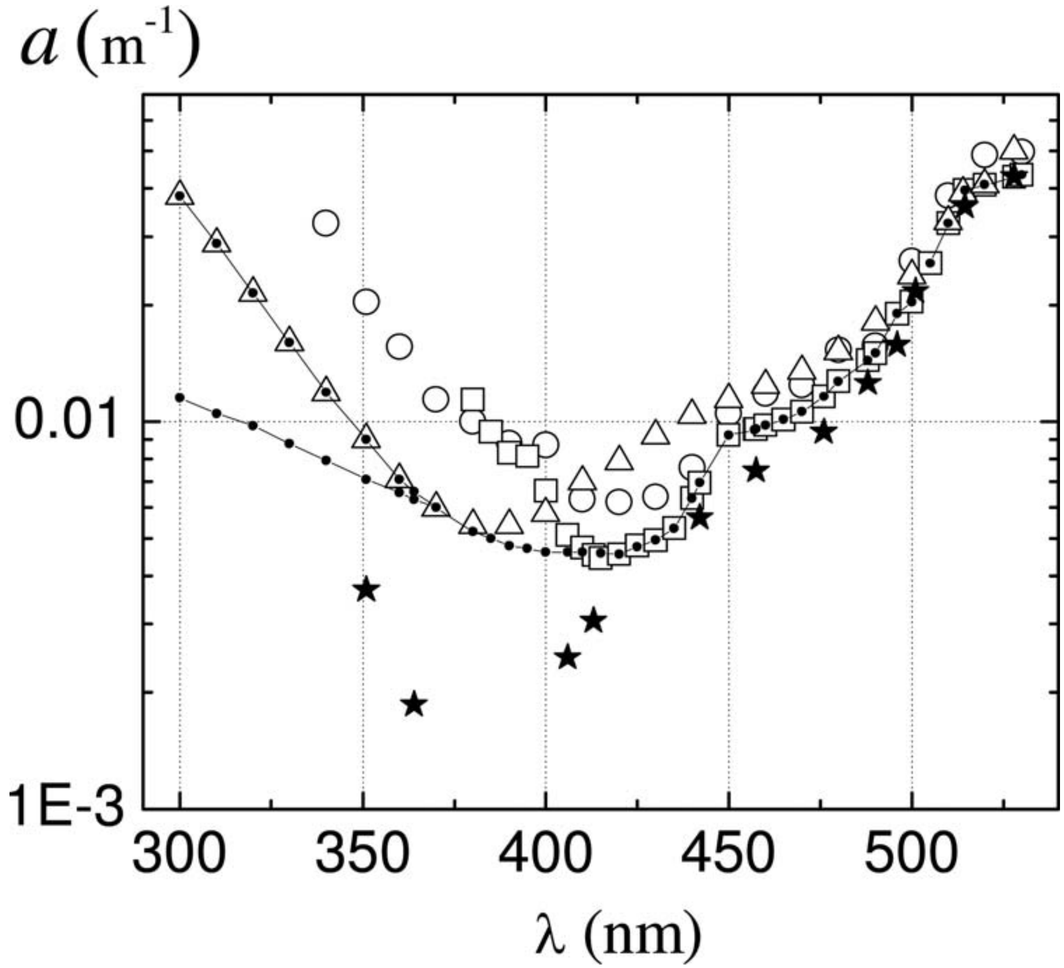
Experimental Z-scan of 1-cm cell containing distilled water measured under the mode-matched (open stars) and mode-mismatched (solid squares) schemes.



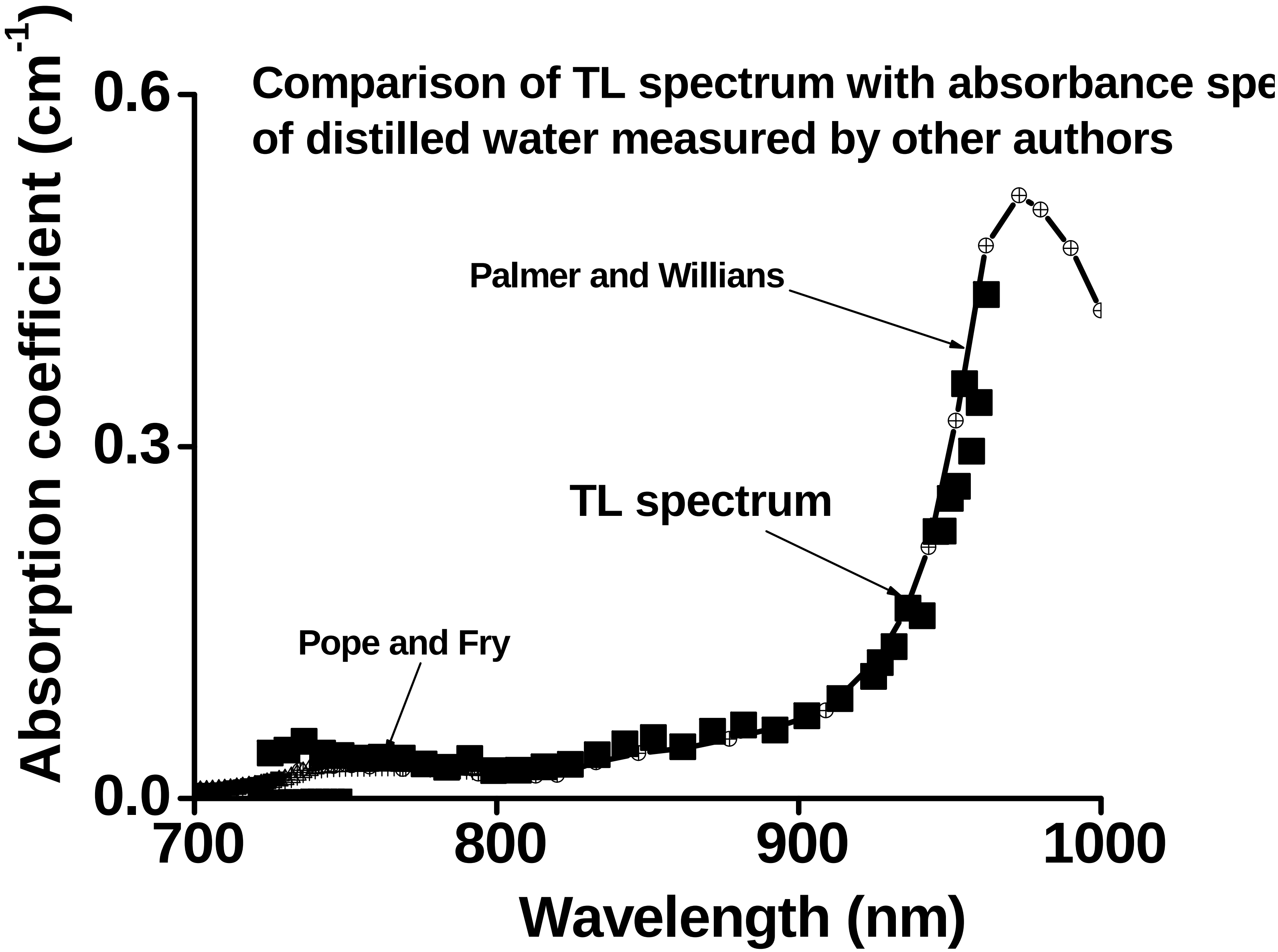
PTL spectra of distilled water measured using the mode-matched (large open stars) and mode-mismatched (large crossed circles) experimental configurations. Results of previous reports on water absorption of different authors have been included (small symbols).

Ultrasensitive spectroscopy of water

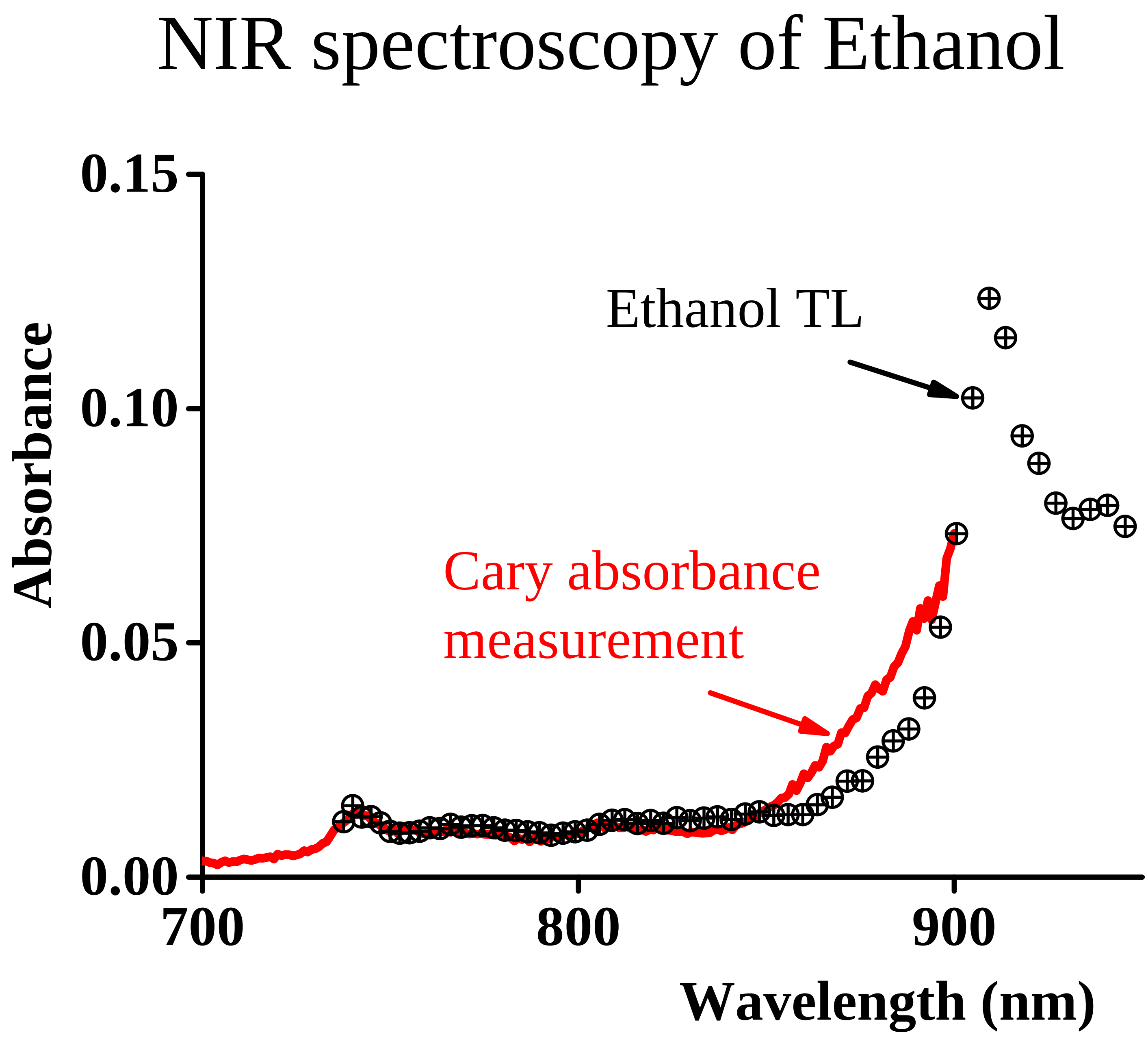
High precision values of absorption of water in the 300-500 nm spectral region



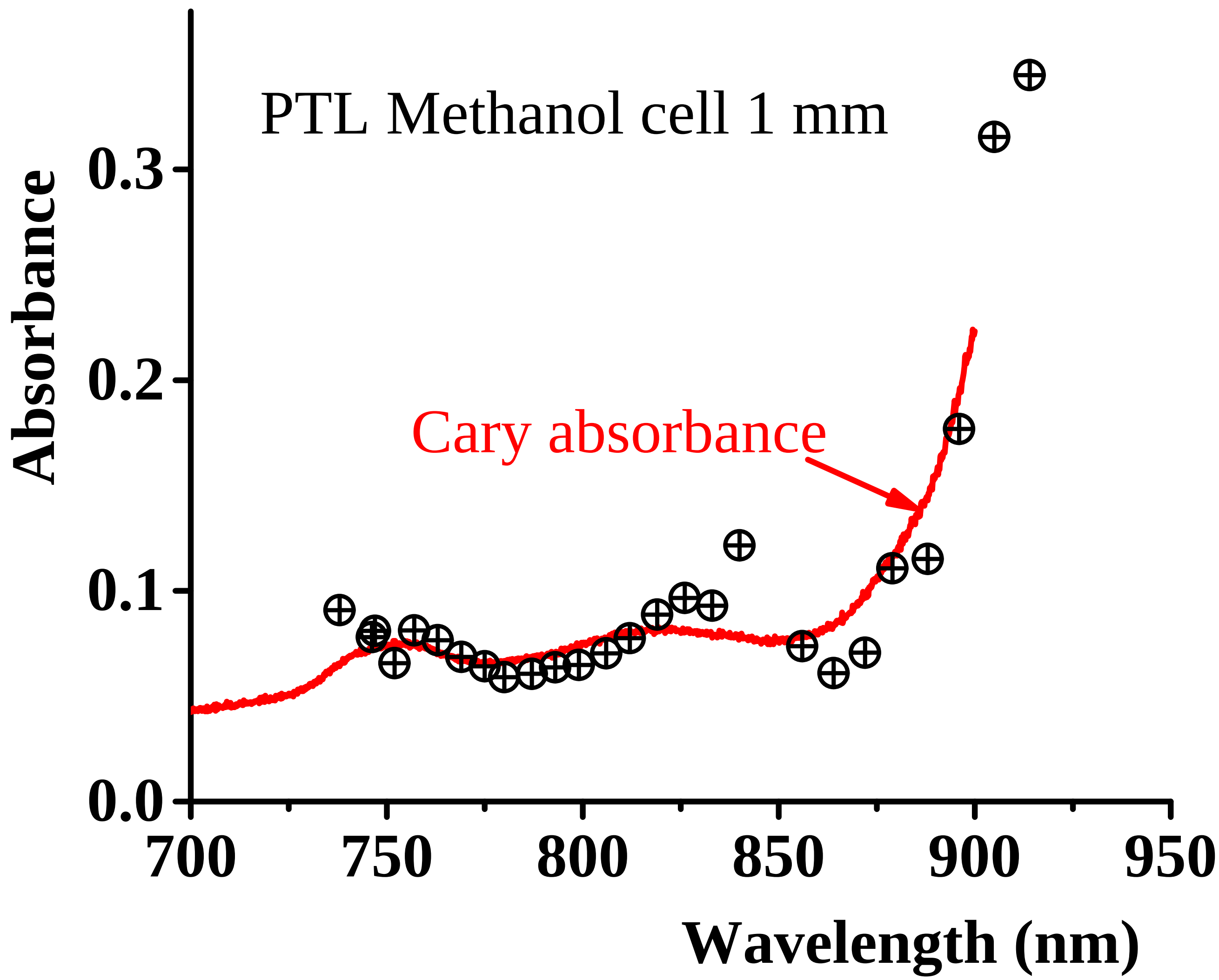
R. A. Cruz, A. Marcano O., C. Jacinto, and T. Catunda, “Ultra-sensitive Thermal Lens Spectroscopy of Water”, Opt. Lett. **34** (12), 1882-1884 (June 15, 2009).

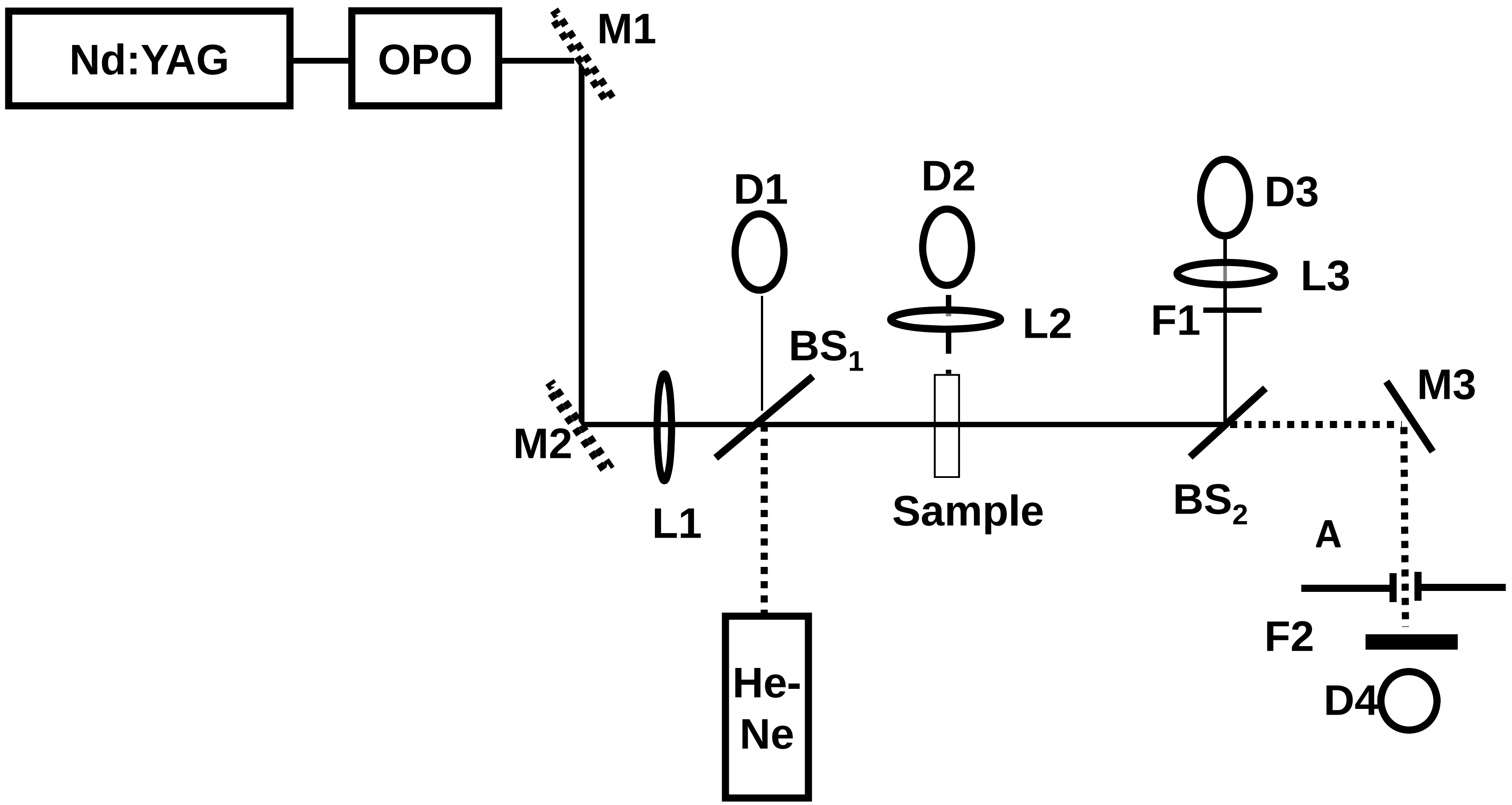


Comparison of TL spectrum with absorbance spe
of distilled water measured by other authors
Absorption coefficient (cm^{-1})
0.6
0.3
0.0
Palmer and Willians
TL spectrum
Pope and Fry
700
800
900
1000
Wavelength (nm)


NIR spectroscopy of Ethanol
Absorbance
0.15
0.10
0.05
0.00
700
800
900
Wavelength (nm)
Ethanol TL
Cary absorbance measurement

NIR of Methanol





Laser based PTL, absorbance ,and fluorescence excitation spectrophotometer.

J. Hung, A. Marcano O., J. Castillo, J. Gonzalez, V. Piscitelli, A. Reyes and A. Fernandez, “Thermal lensing and absorbance spectra of a fluorescent dye”, Chem. Phys. Lett. **386**, 206-210

. Absorbance (crossed circles), fluorescence excitation (crossed stars) and TL spectra (solid triangles) of a 5 10^{-6} M ethanol solution of Rhodamine 6G. The solid line is the absorbance spectrum of the same sample obtained using a spectrophotometer.

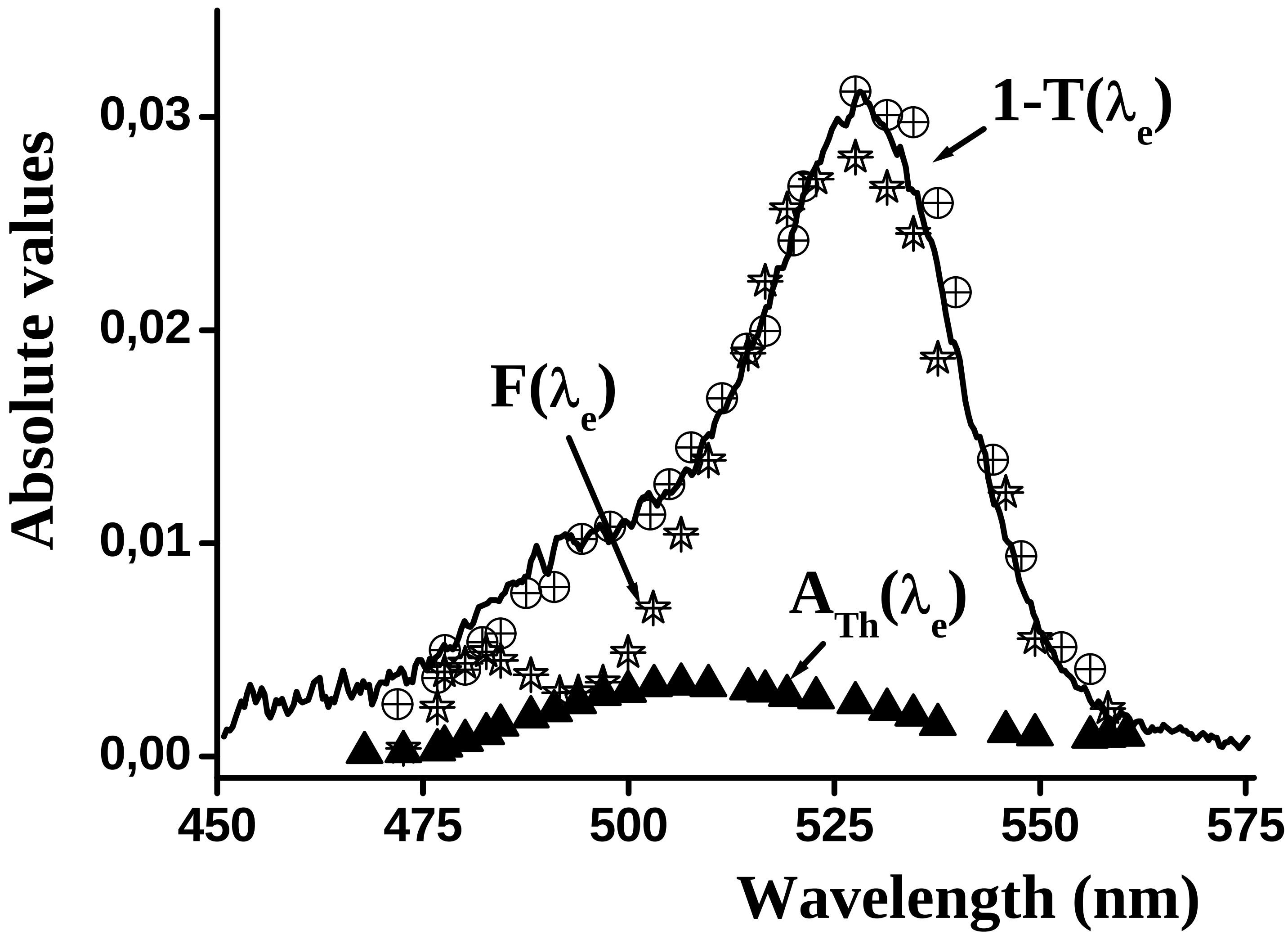
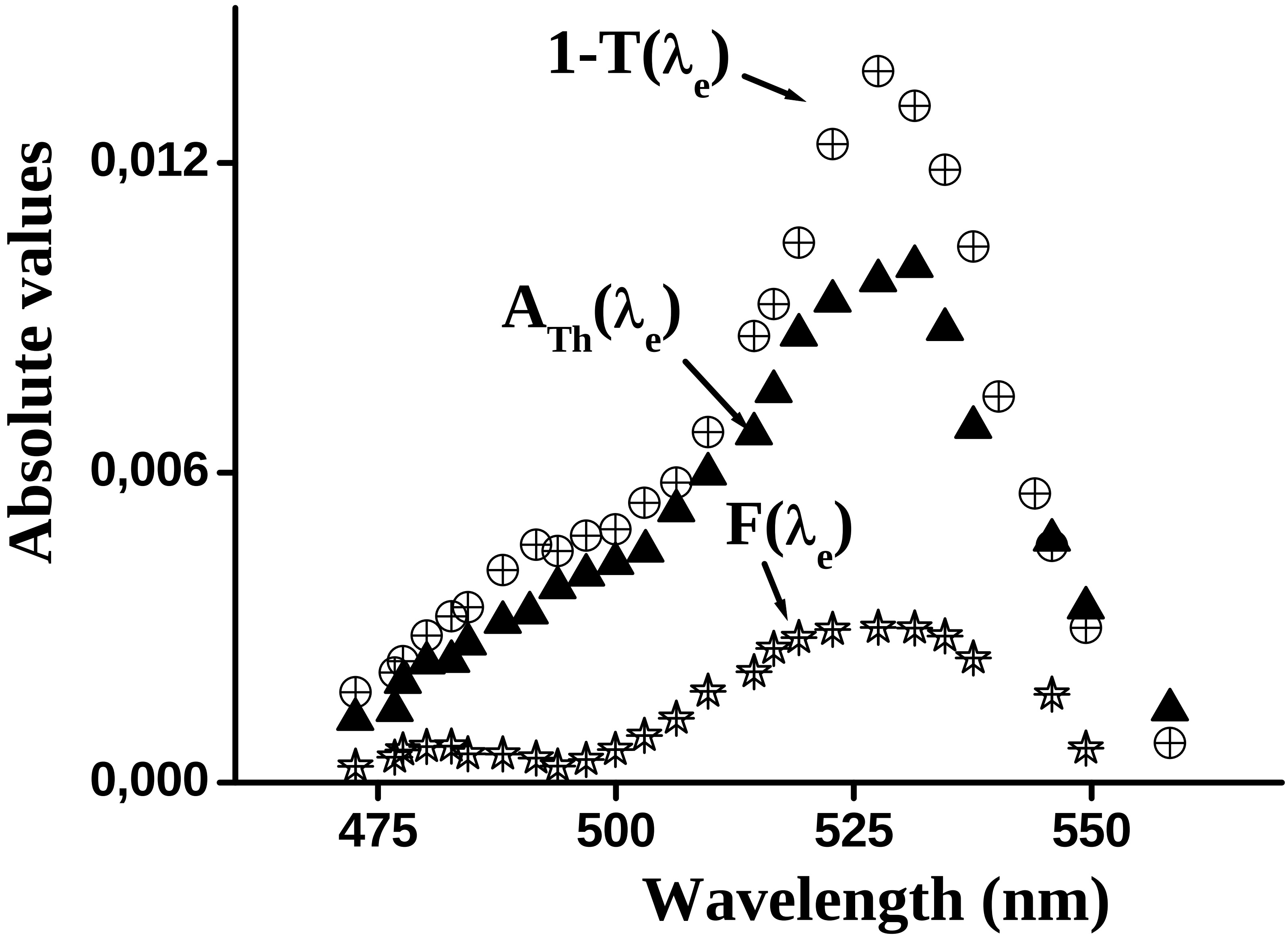
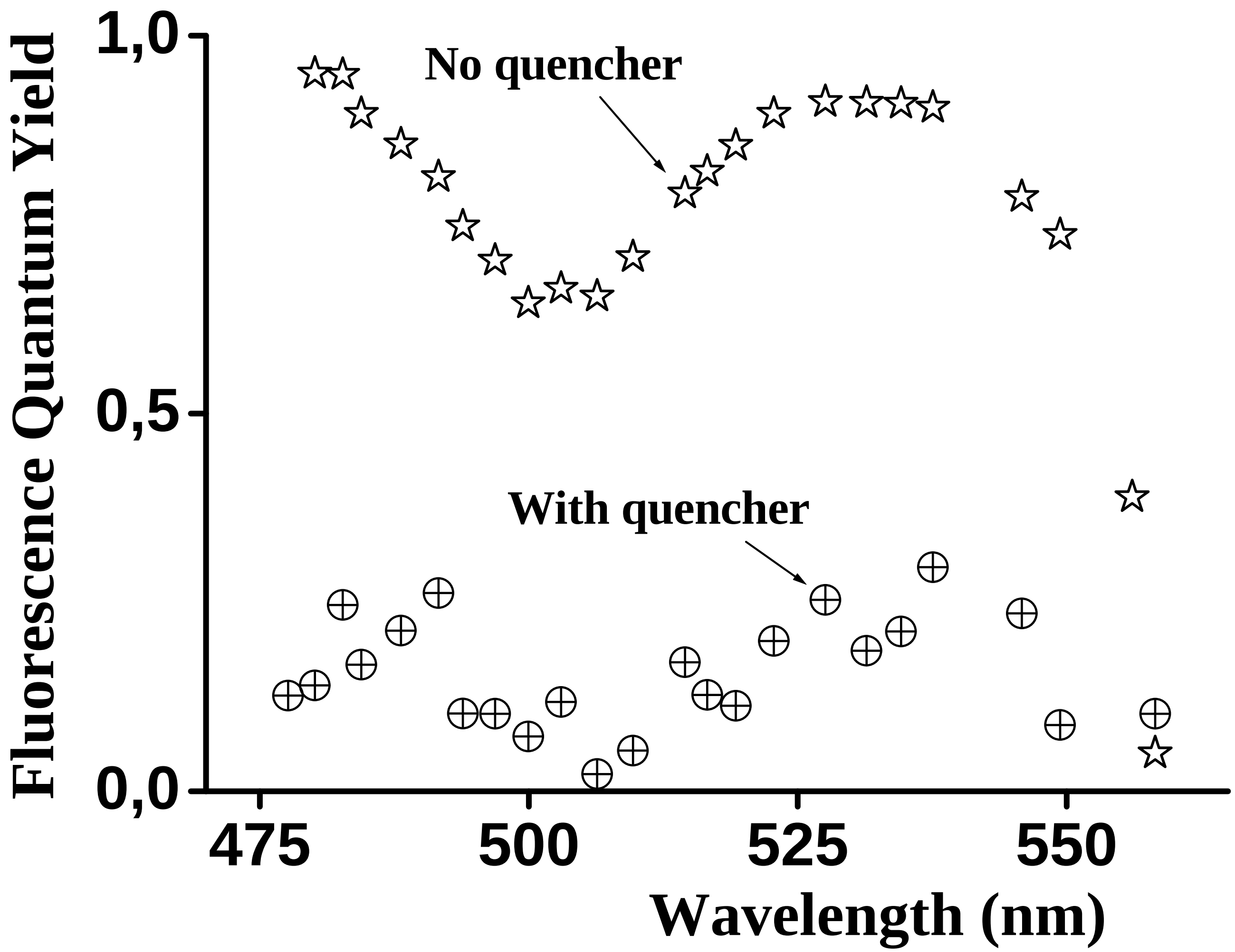


Figure 2. Hung et al.

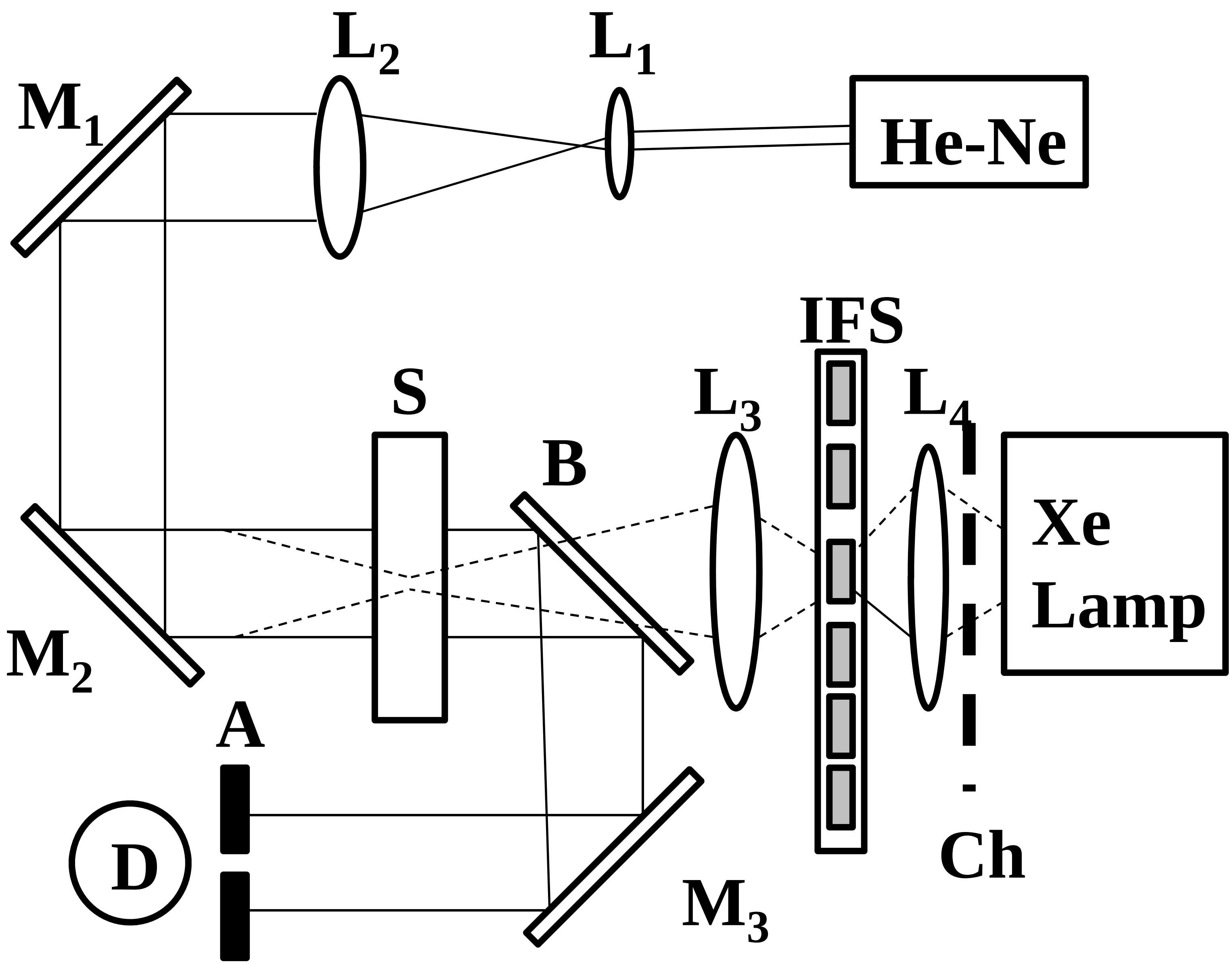


Absorbance (crossed circles), fluorescence excitation (crossed stars) and TL spectra (solid triangles) of the same sample of previous slide after adding of the quencher (KI).

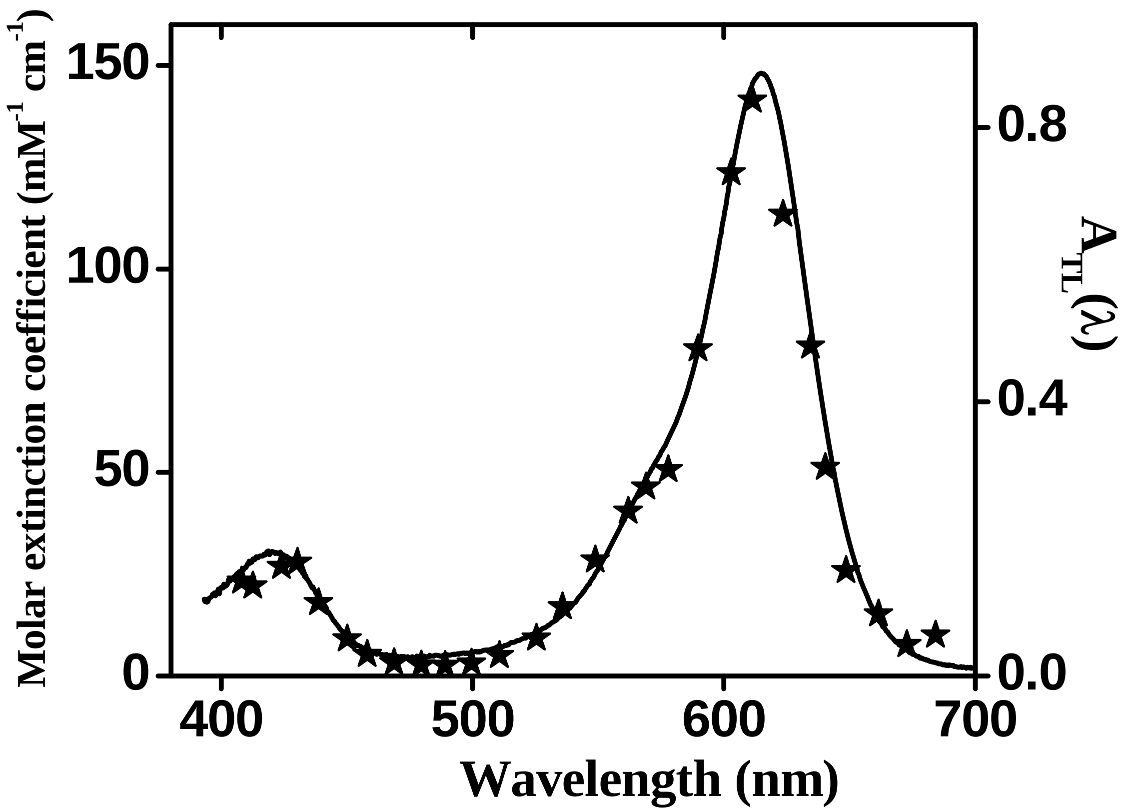


Fluorescence quantum yield spectrum of the 5 10^{-6} M ethanol solution of Rhodamine 6G in presence of high fluorescence and in the presence of fluorescence quenching.

White light photothermal lens spectrophotometer



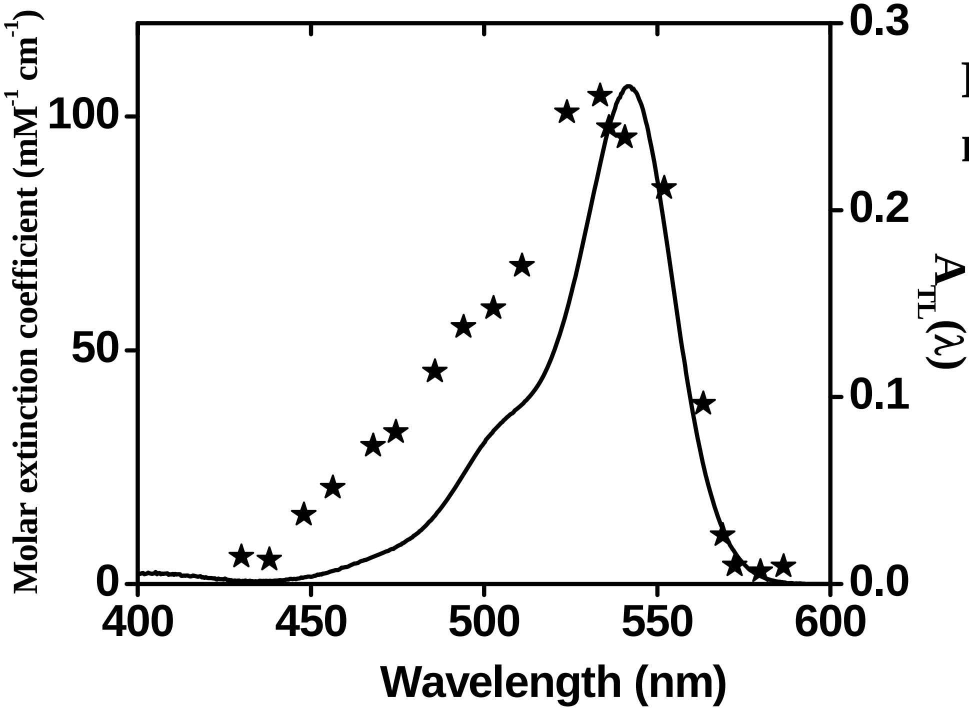
PTL spectrum of a non-fluorescent dye



PTL spectrum of 0.125 mM solution of Malachite green in ethanol.
There is coincidence with the absorbance spectrum.

A. Marcano O., J. Ojeda and N. Melikechi, "Absorption spectra of dye solutions measured using a white-light thermal lens spectrophotometer", Appl. Spectros. **60** (5), 560-563 (2006).

PTL of a fluorescent dye

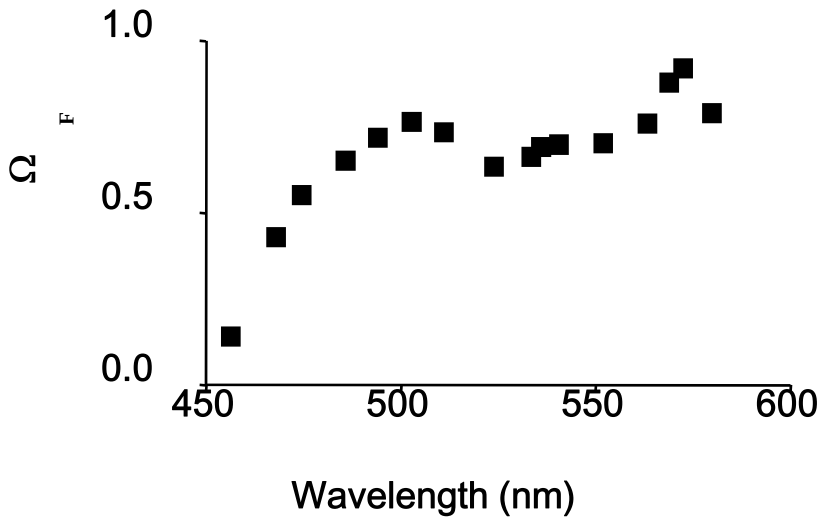


PTL and absorbance spectra of a 50 mM solution of R6G in ethanol.

Because of fluorescence both spectra are different. This property of PTL spectroscopy can be used for measuring the quantum yield of fluorescence

Quantum yield of fluorescence

$$\Omega_F = (\lambda_F/\lambda)(1 - A_{TL}(\lambda)/(1 - \exp(\alpha(\lambda)L)))$$



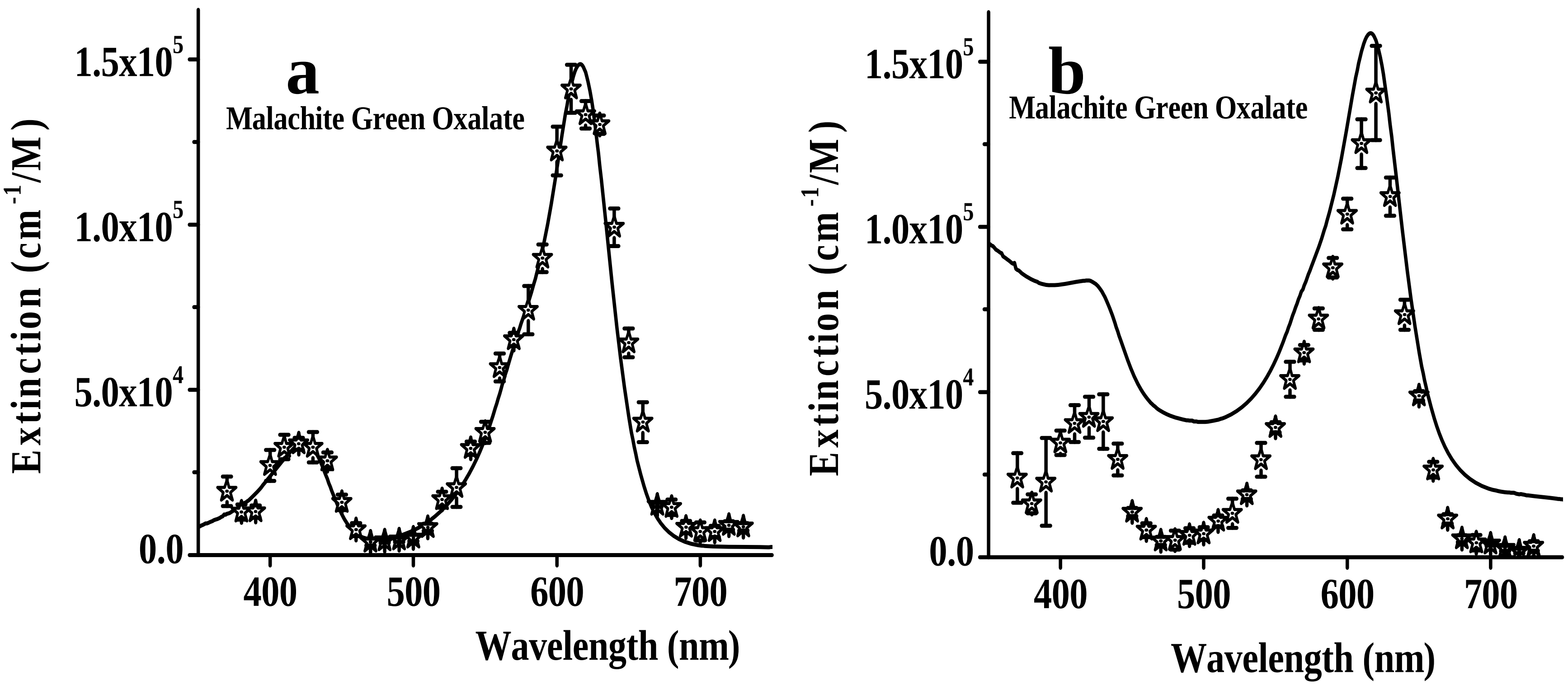
$A_{TL}(\lambda)$ **PTL absorbance**

$\alpha(\lambda)L$ **absorbance**

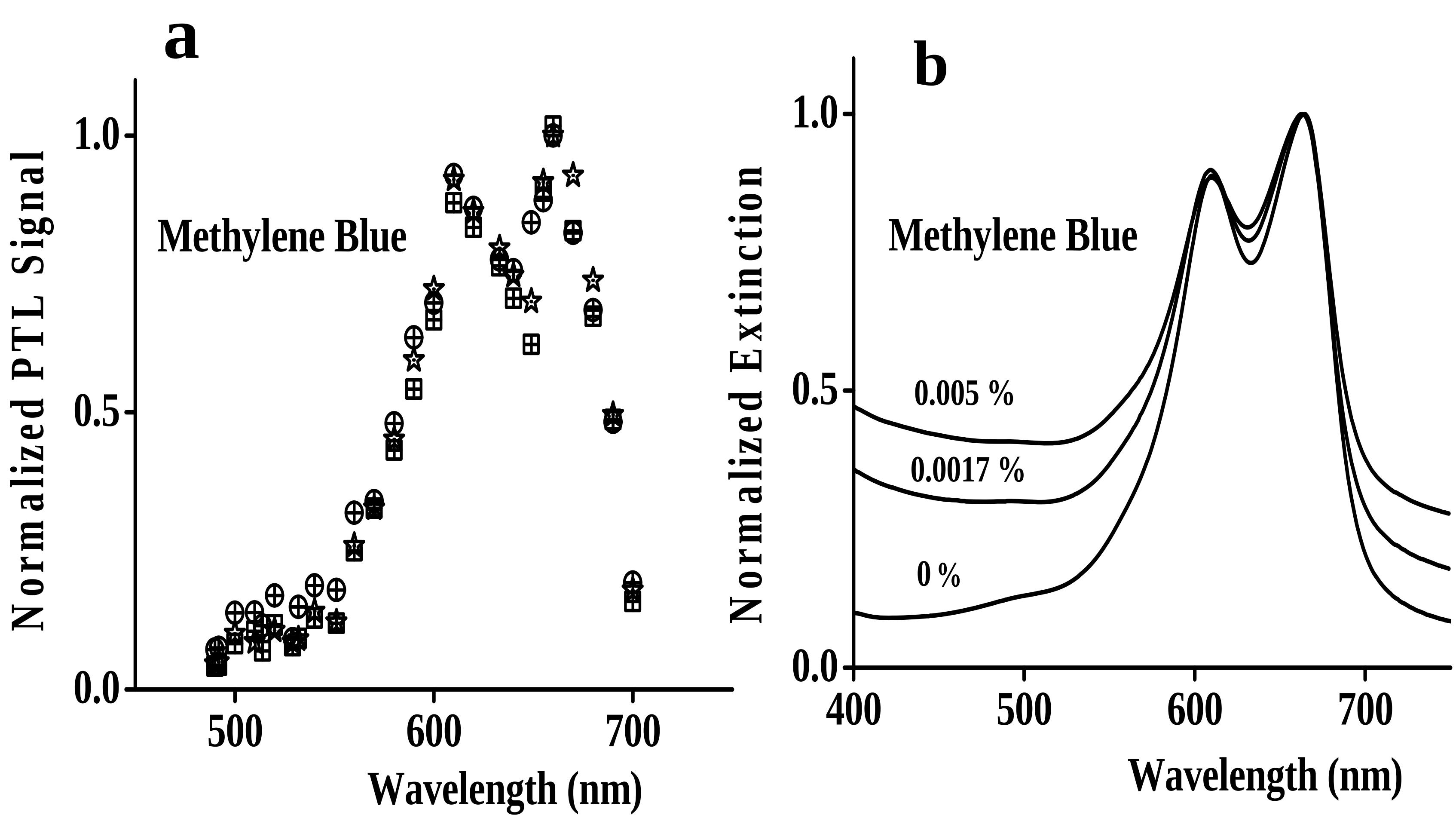
λ_F **Average wavelength of fluorescence**

PTL spectroscopy of scattering samples

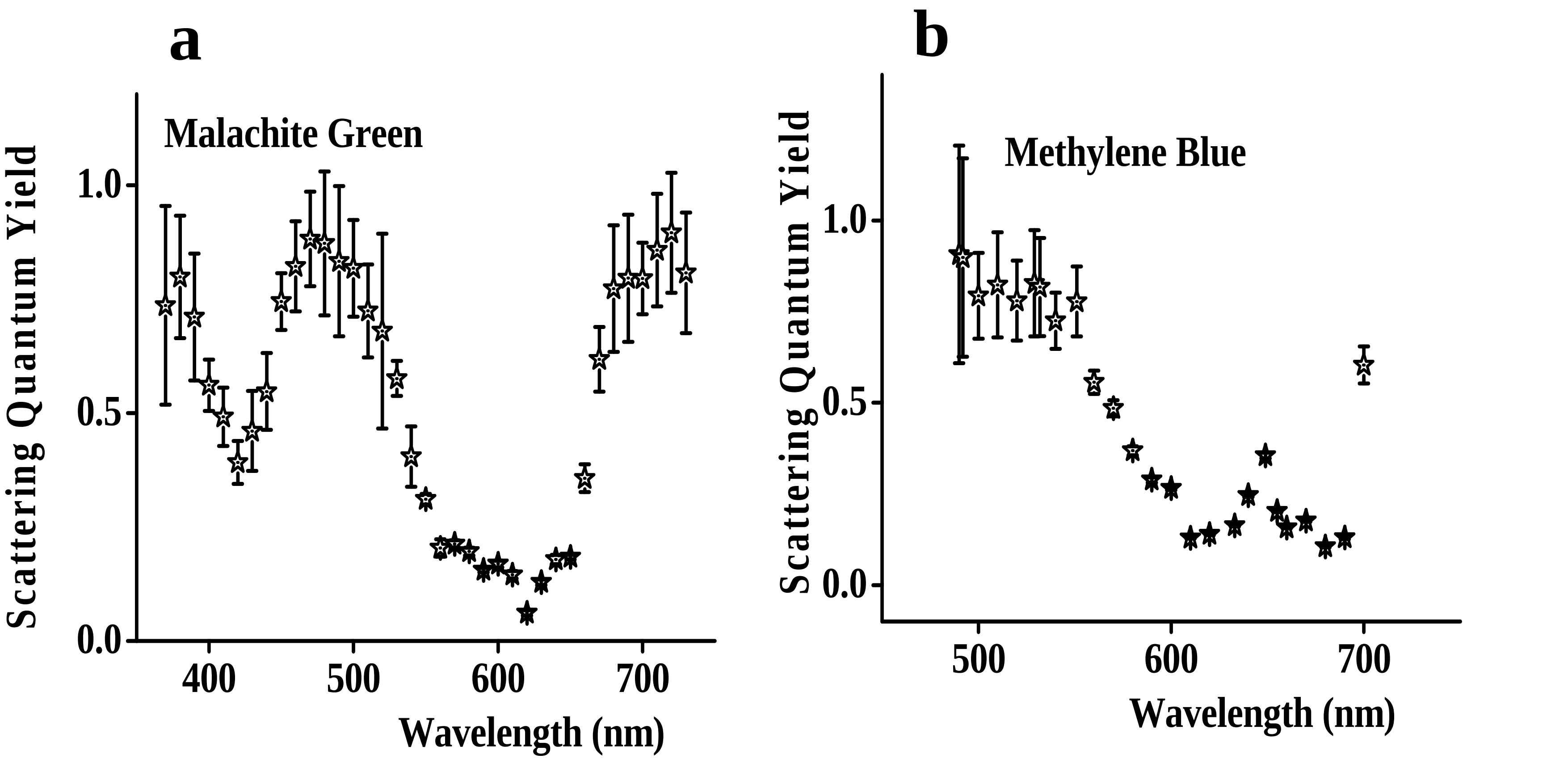
A. Marcano O., S. Alvarado, J. Meng, D. Caballero, E. Marin and R. Edziah, Applied Spectroscopy, 68 (6), 680-685, June 2014. DOI: 10.1366/13-07385.



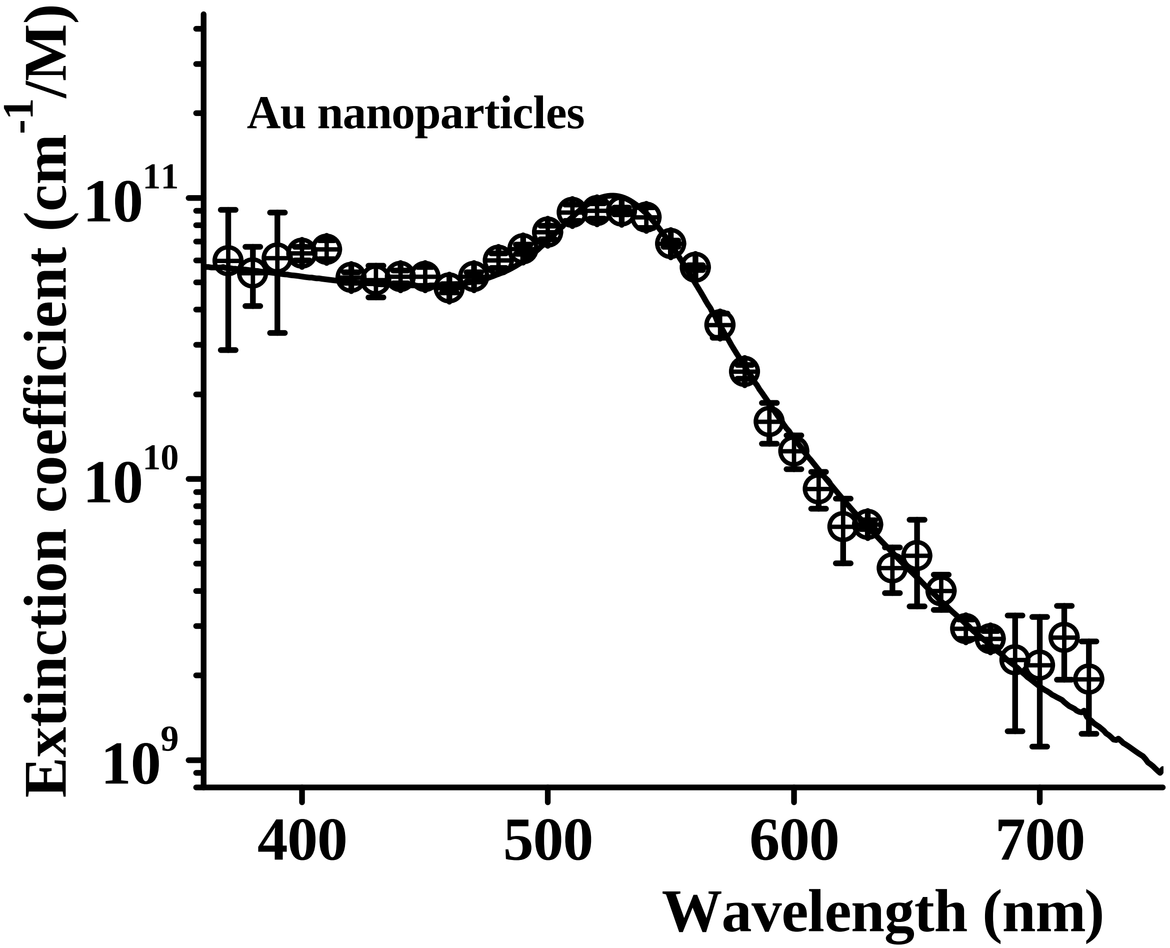
a- PTL and extinction spectra of Malachite Green Oxalate with no polystyrene microbeads added; b- PTL and extinction spectra of Malachite Green Oxalate containing polystyrene microbeads at concentration of *0.005%* by weight. The standard deviation is estimated averaging over 5 different experiments.



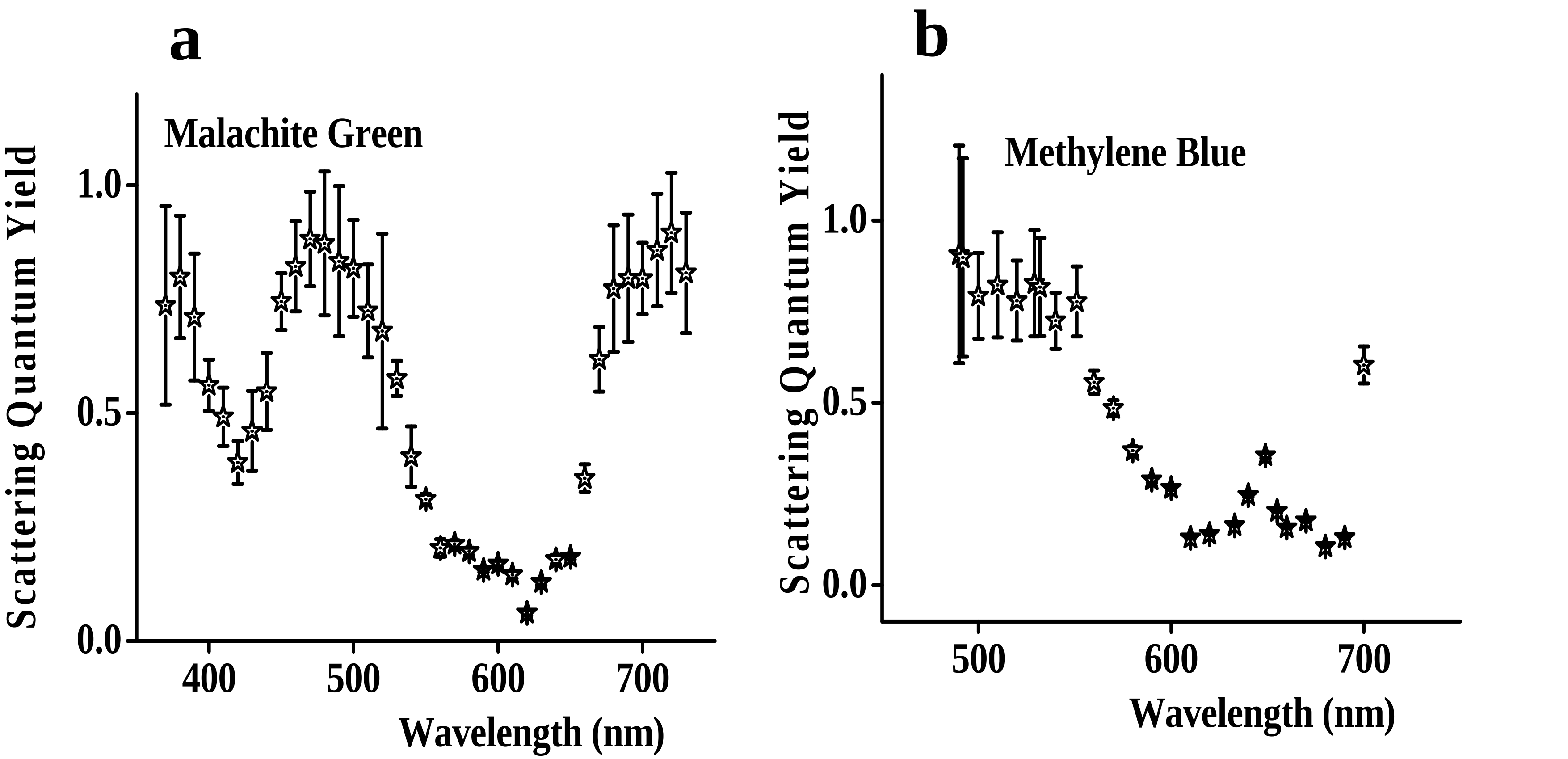
a - Normalized PTL spectra of Nile Blue with polystyrene microbeads added at concentration of *0* (crossed circles), *0.0017%* (stars) and *0.005%* (crossed squares) by weight; b- Normalized extinction spectra of Nile Blue containing polystyrene microbeads at concentration of *0*, *0.0017%* and *0.005%* by weight as indicated. The standard deviation is estimated averaging over 5 different experiments.



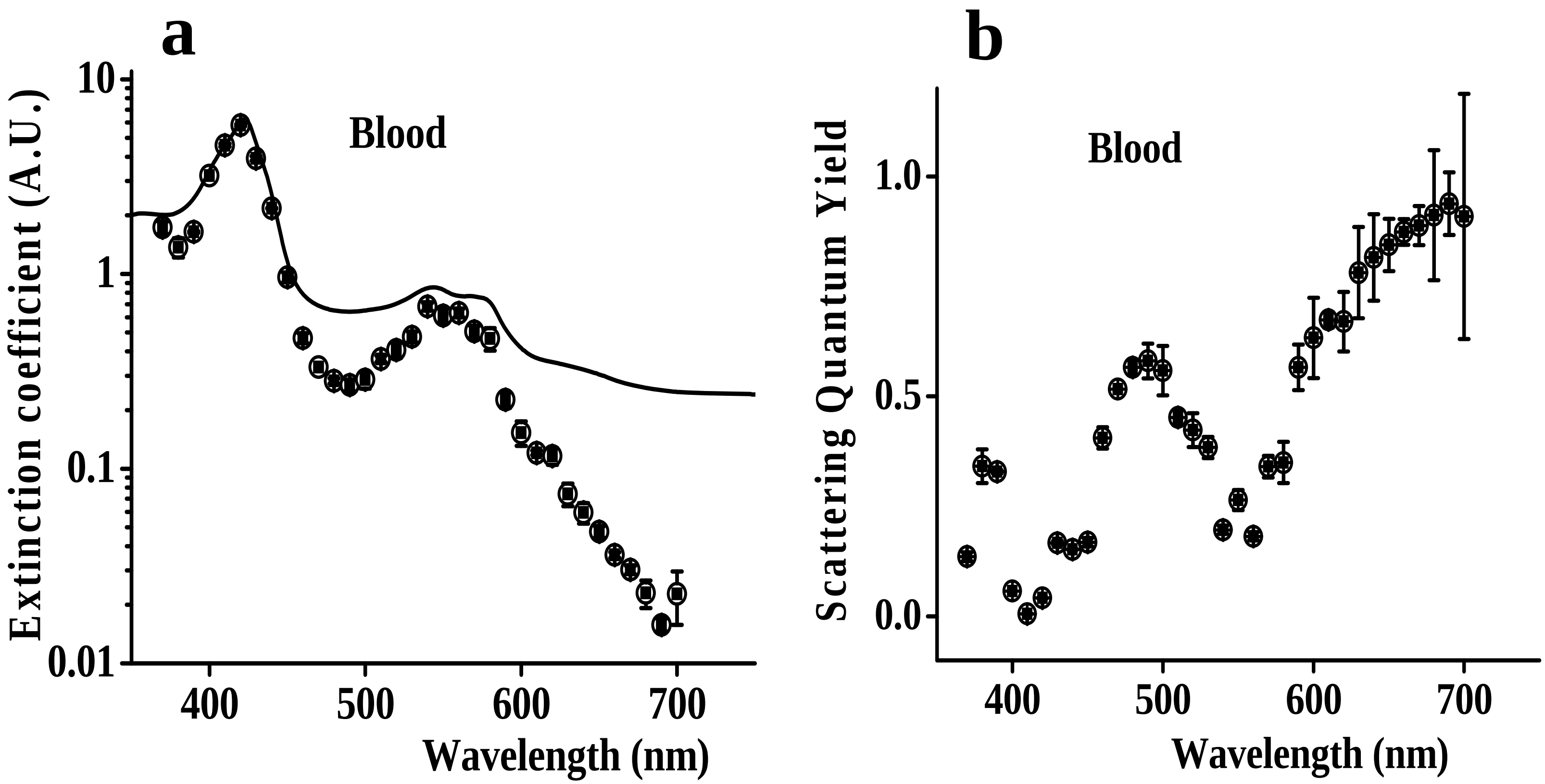
a- Scattering quantum yield of the Malachite Green Oxalate sample with added polystyrene microparticles at 0.005 % concentration by weight; b- Scattering quantum yield of the Nyle Blue sample with added polystyrene microparticles at 0.005 % by weight. The standard deviation is estimated averaging over 5 different experiments.



Extinction (solid line) and PTL (crossed circles) spectra of a solution of 50-nm diameter gold nanoparticles at concentration of 1 mg/mL. The standard deviation is estimated averaging over 5 different experiments.

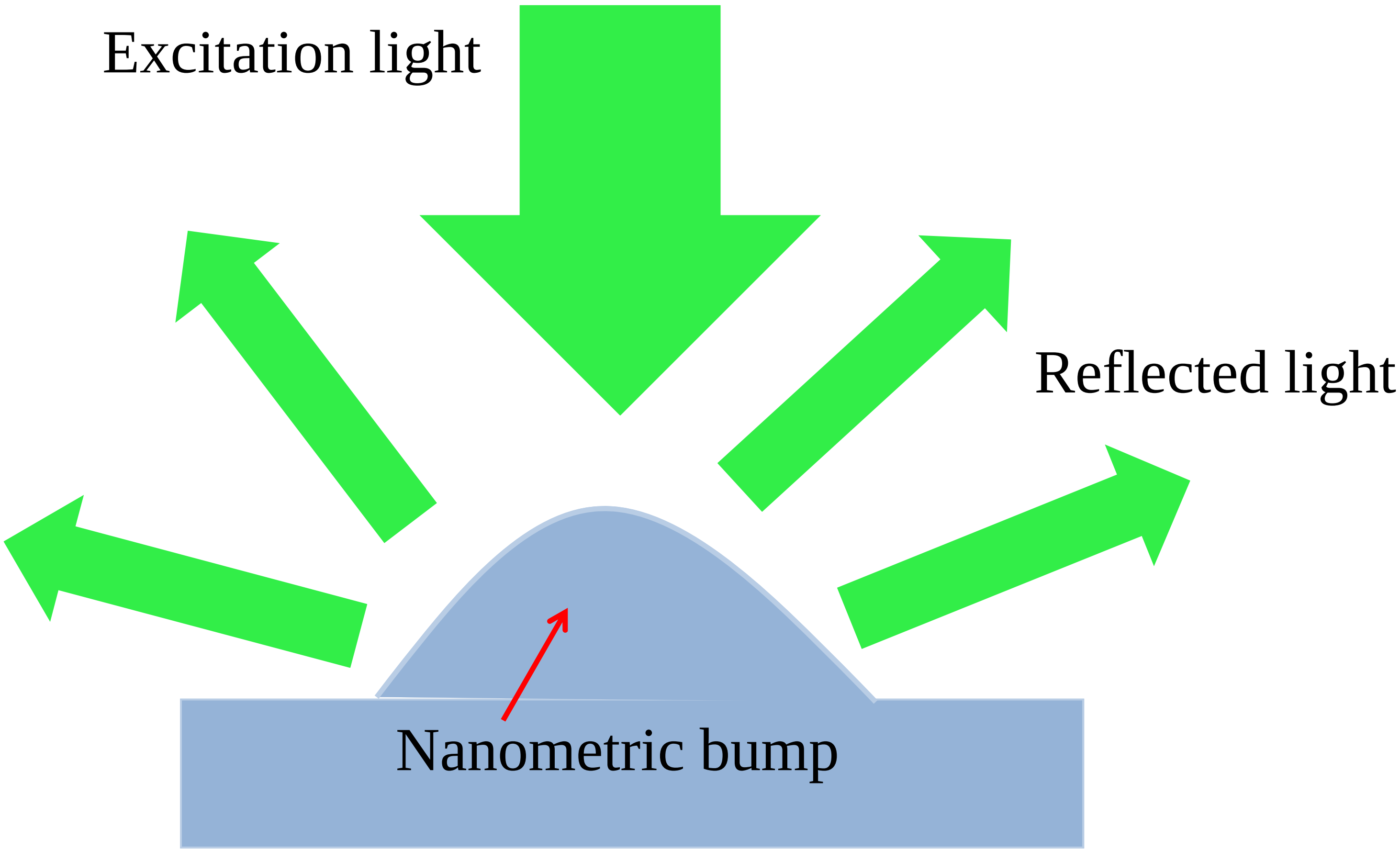


a- Scattering quantum yield of the Malachite Green Oxalate sample with added polystyrene microparticles at 0.005 % concentration by weight; b- Scattering quantum yield of the Nyle Blue sample with added polystyrene microparticles at 0.005 % by weight. The standard deviation is estimated averaging over 5 different experiments.

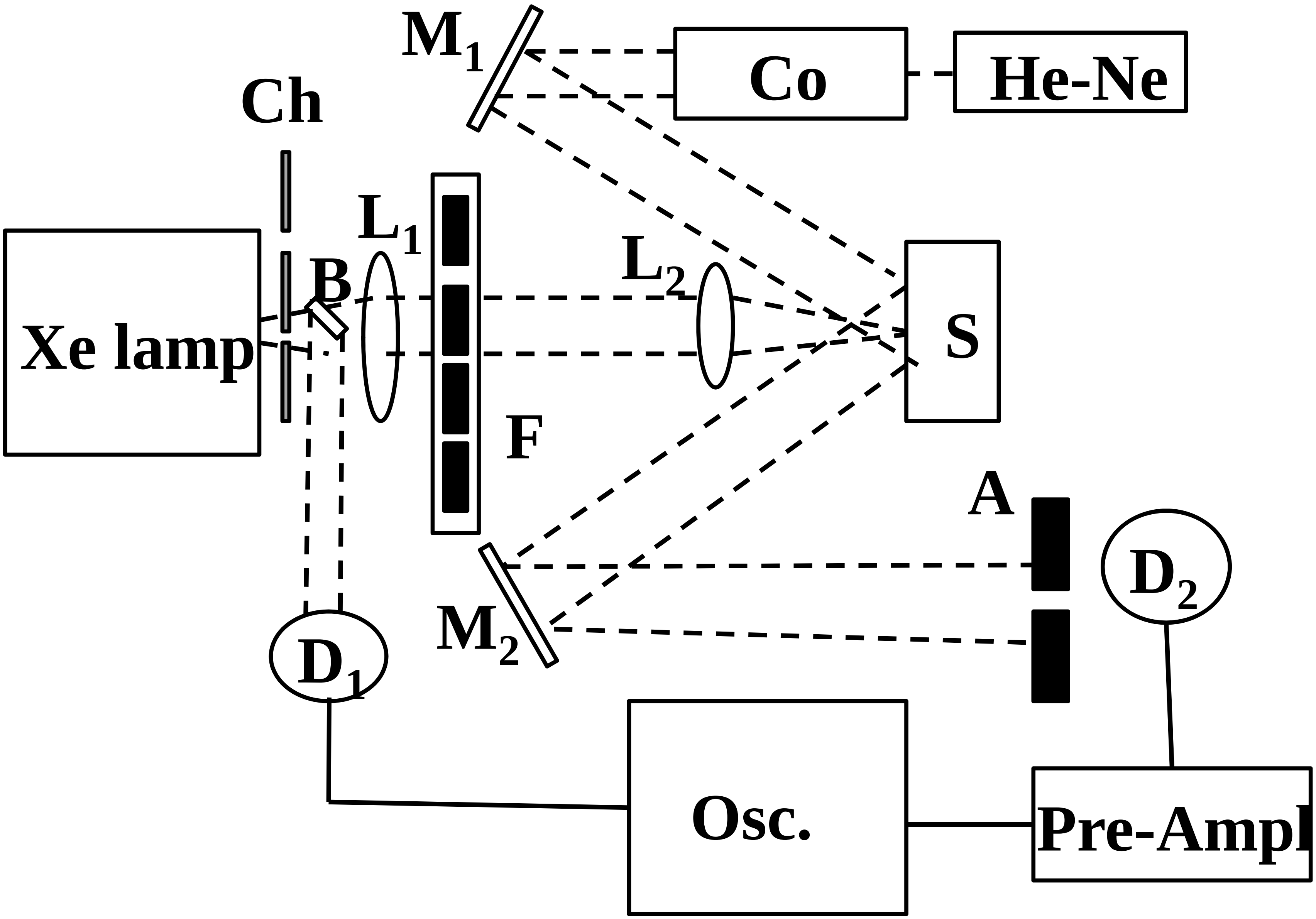


a- Extinction (solid line) and PTL (crossed circles) spectra of a blood sample; b- Scattering quantum yield of the same blood sample. The standard deviation is estimated averaging over 5 different experiments.

Photothermal mirror effect



White-light photothermal mirror spectrophotometer



The signal is defined as

$$S(\lambda) = \frac{T(\lambda) - T_o}{T_o}$$

$T(\lambda)$ is the transmission through the aperture of the probe light in the presence of the pump beam.

T_o is the transmission through the aperture of the probe light in the absence of the pump beam.

A model based on the simultaneous resolution of the thermo-elastic deformation of the surface and thermal diffusivity equation predicts that

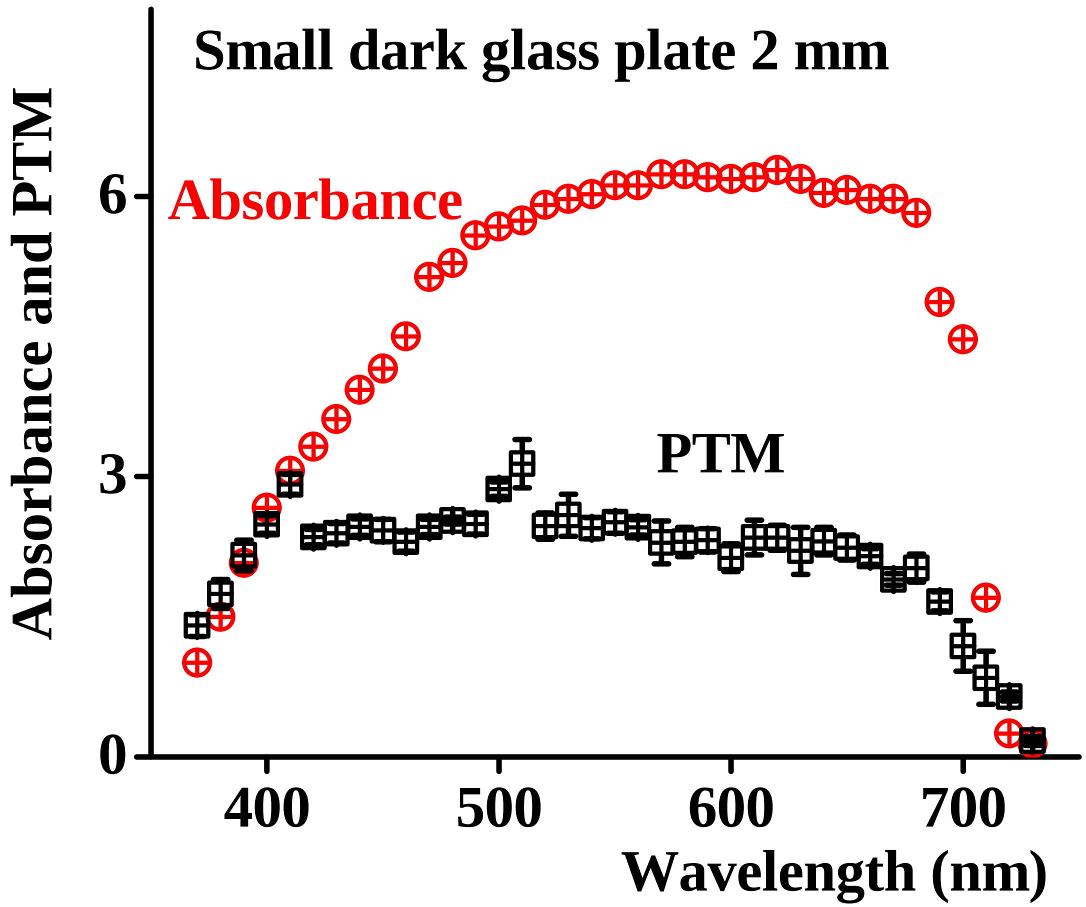
$$S(\lambda) = K \cdot P(\lambda) \cdot \Psi(\lambda)$$

$\Psi(\lambda)$ is the fraction of absorbed energy used to generate heat

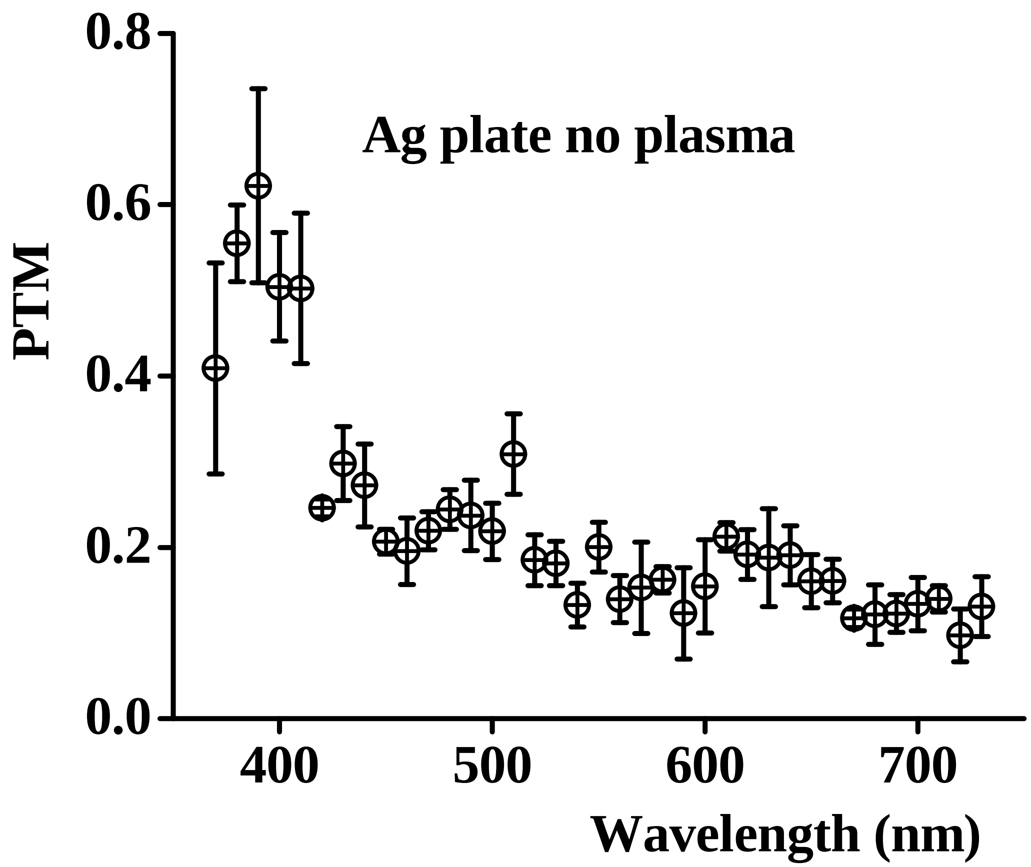
$P(\lambda)$ is the power of the pump light

K is a proportionality coefficient that does not depend on λ

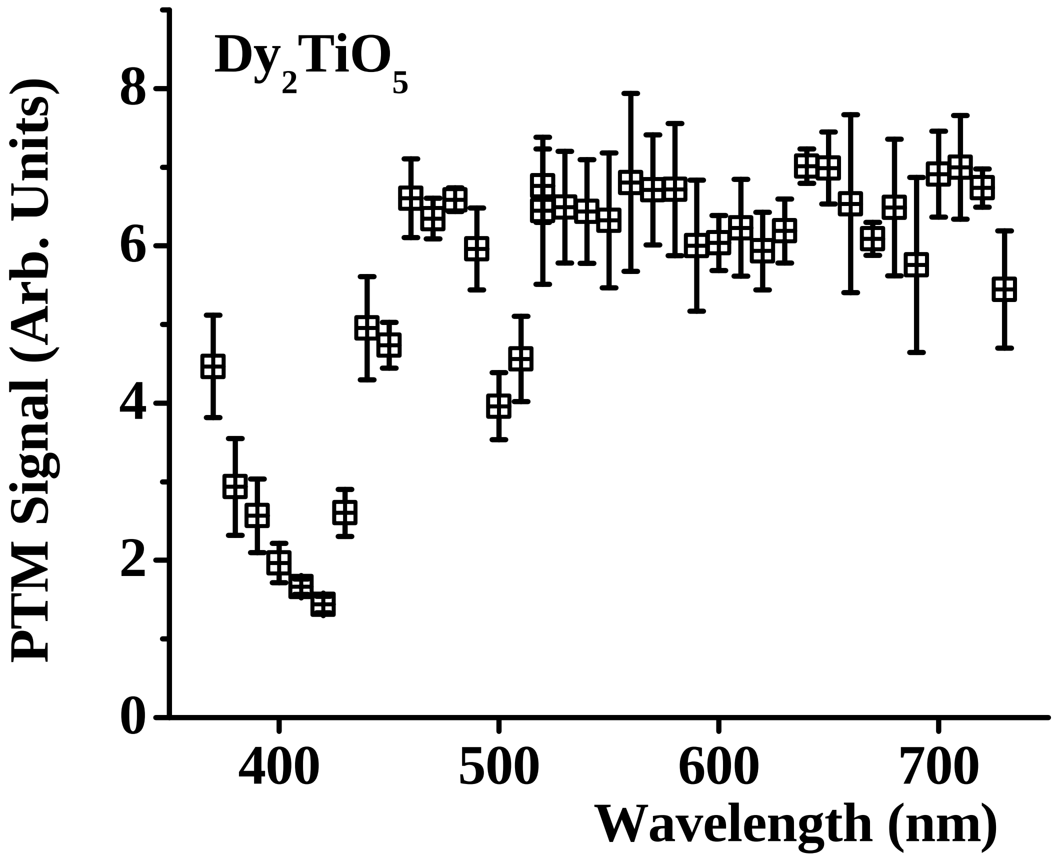
$\Psi(\lambda)$ ➡ PTM spectrum



PTM (black crossed squares) and absorbance (red crossed circles) of a glass plate



PTM spectra of a film made using the deposits from a silver nanoparticle solution



PTM spectrum of the dysprosium titanate sample

Conclusions

Photothermal spectroscopy (PT) is a new spectroscopic method that measures the ability of matter to produce heat following the absorption of light.

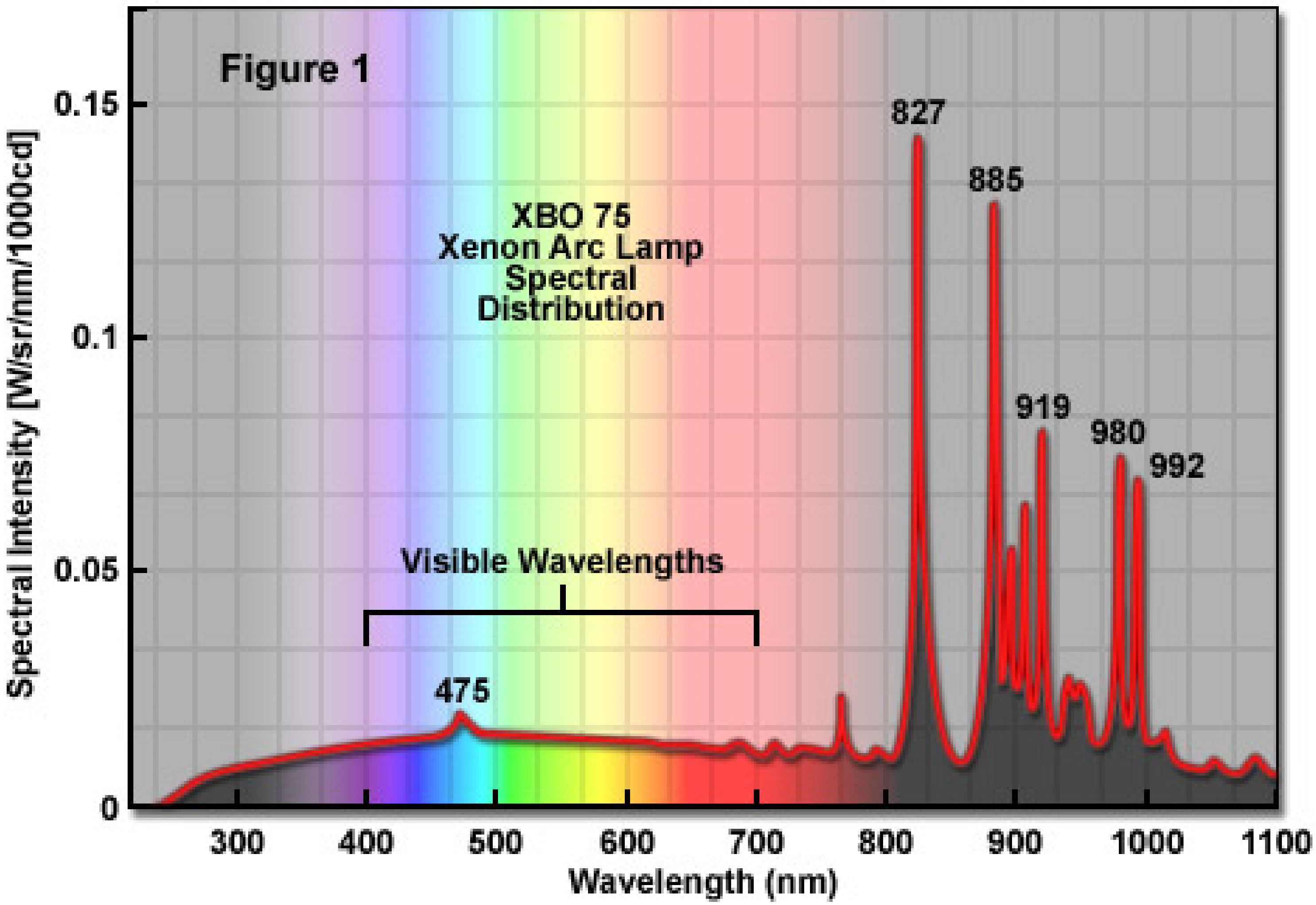
PT spectra and absorbance spectra coincide for samples with 100 % thermal yield.

Advantages

- High sensitive
- Universality (any sample, any spectral region).
- Scattering and fluorescence free
- Only visible sensor technology required (no IR or UV sensors needed)
- Remote sample analysis possible
- Traditional and modern light source technology can be adapted.
- Low cost.

Light Sources for PT Spectroscopy

Arc lamps



http://zeiss-campus.magnet.fsu.edu/print/lightsources/xenonarc-print.htm

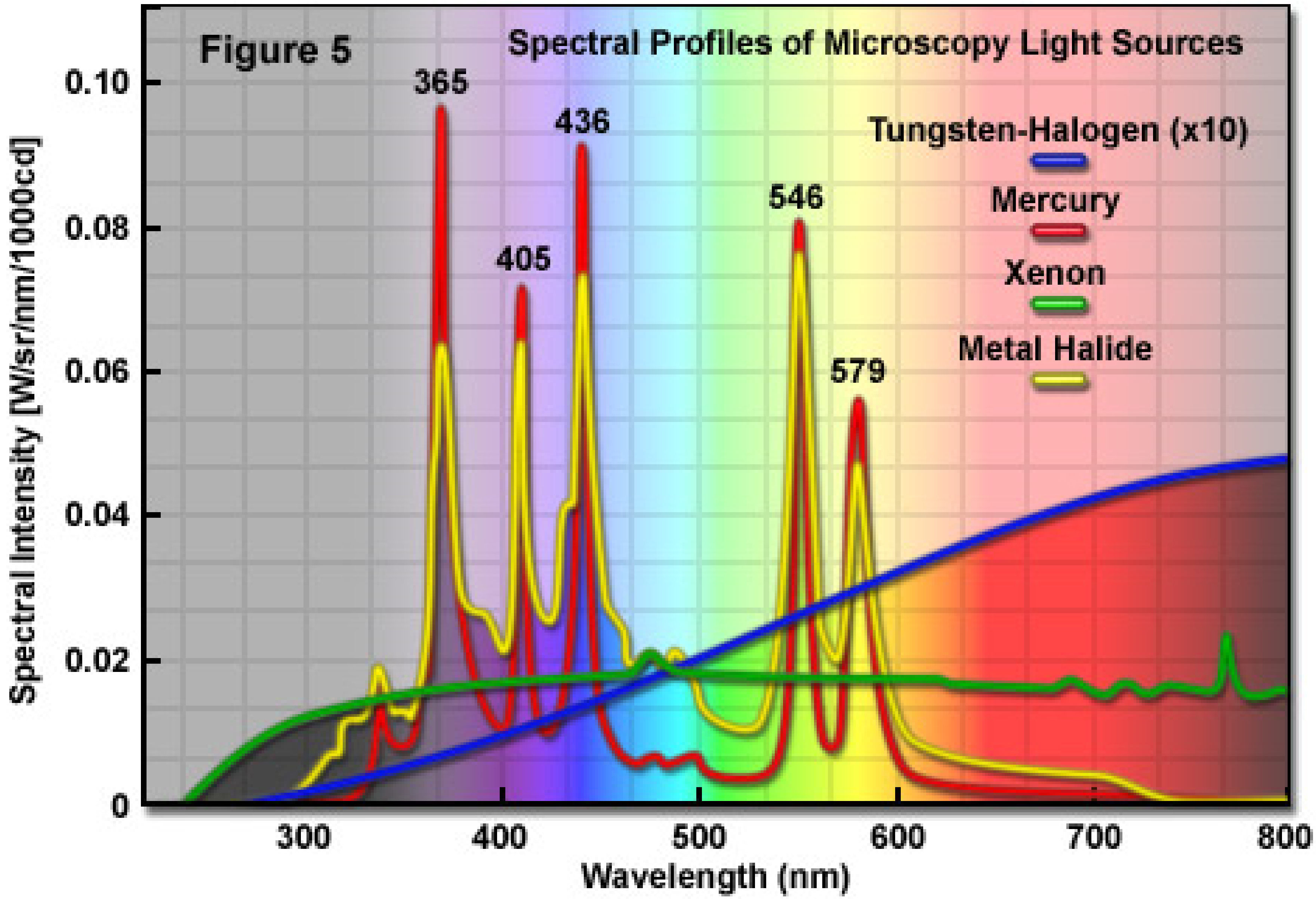


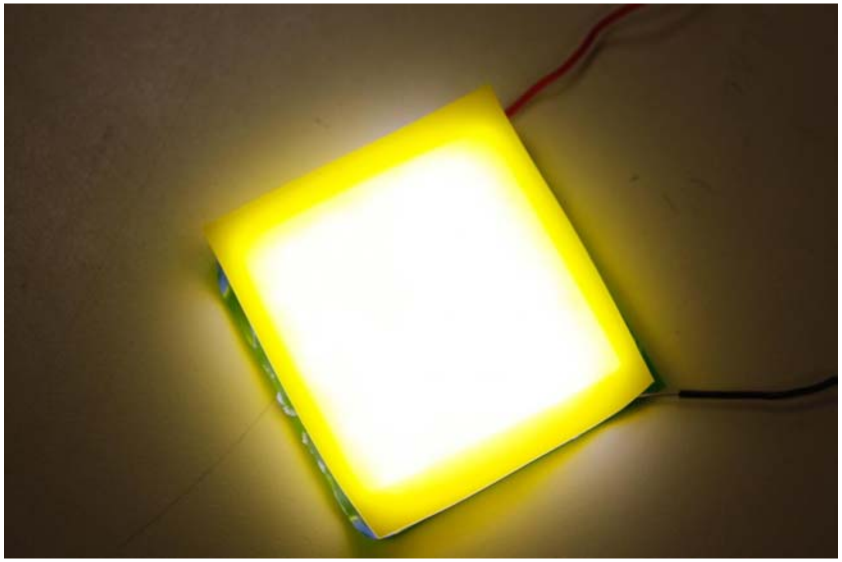
Figure 5
Spectral Profiles of Microscopy Light Sources
365
405
436
546
579
Tungsten-Halogen (x10)
Mercury
Xenon
Metal Halide
Spectral Intensity [W/sr/nm/1000cd]
0.10
0.08
0.06
0.04
0.02
0
300
400
500
600
700
800
Wavelength (nm)

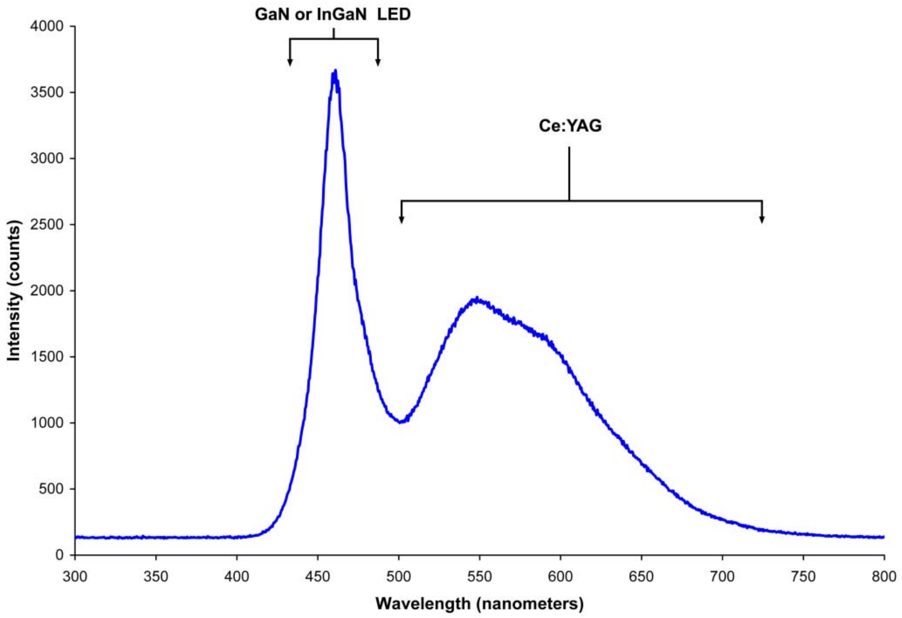
High Intensity Tunable Light Source

22K$

www.newport.com

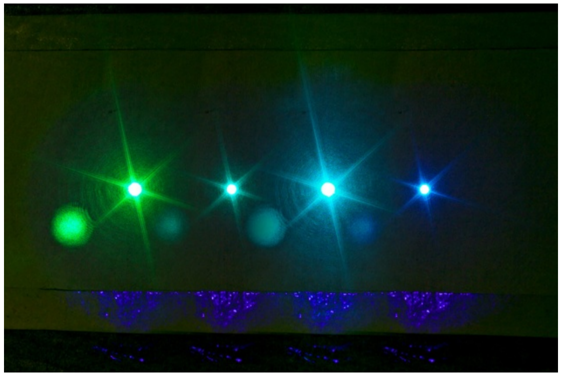
White Leds

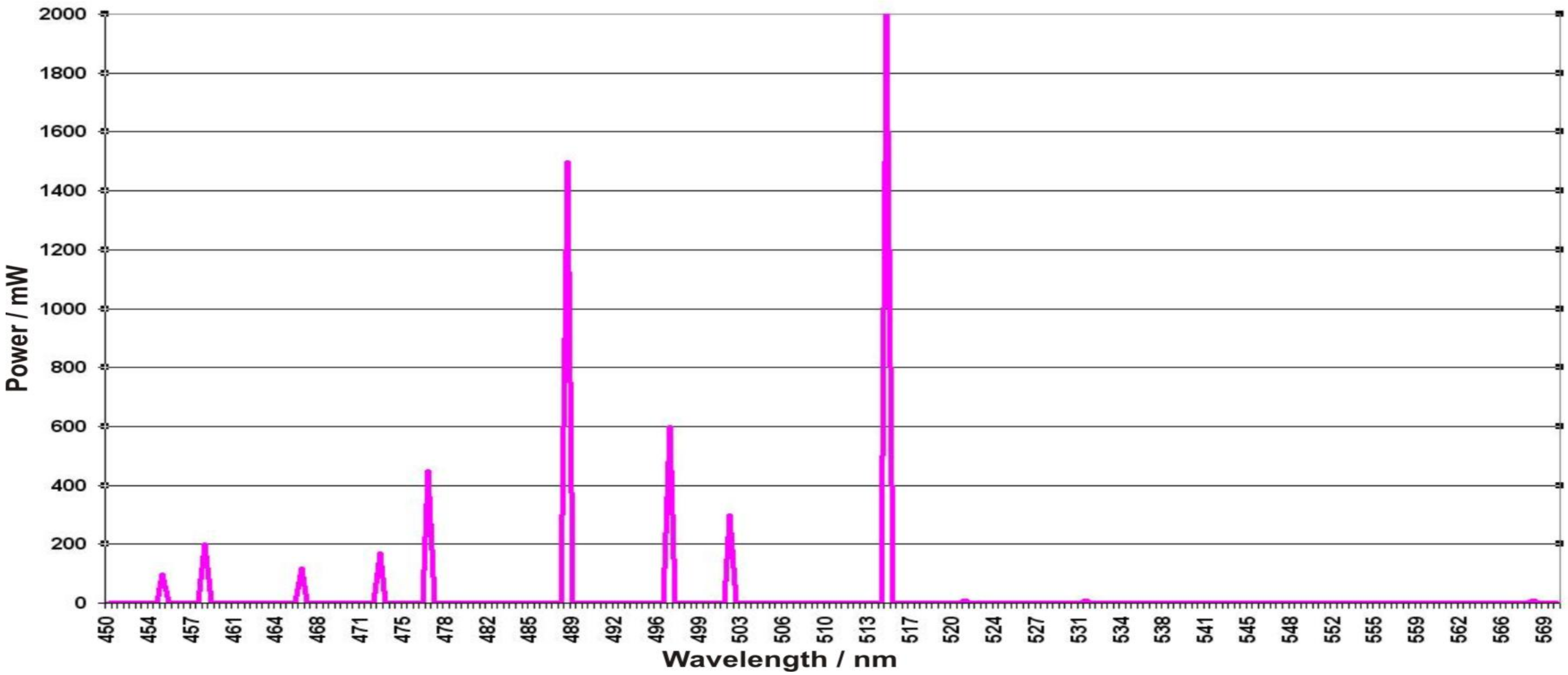




10$ on ebay

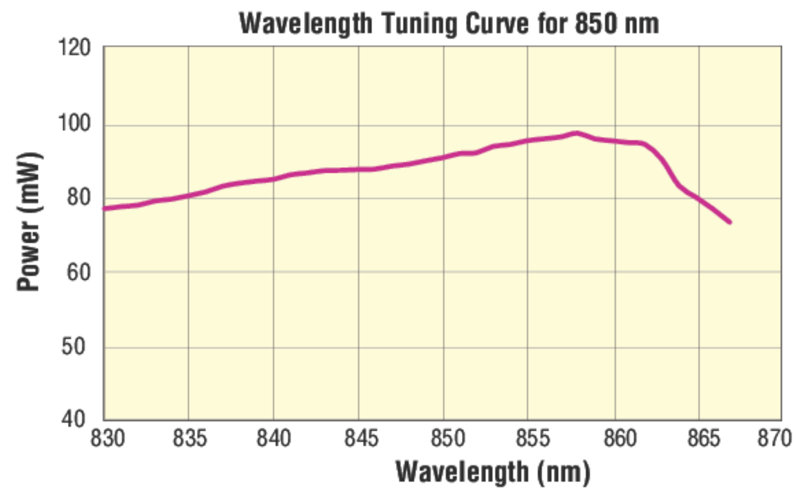
The Argon laser





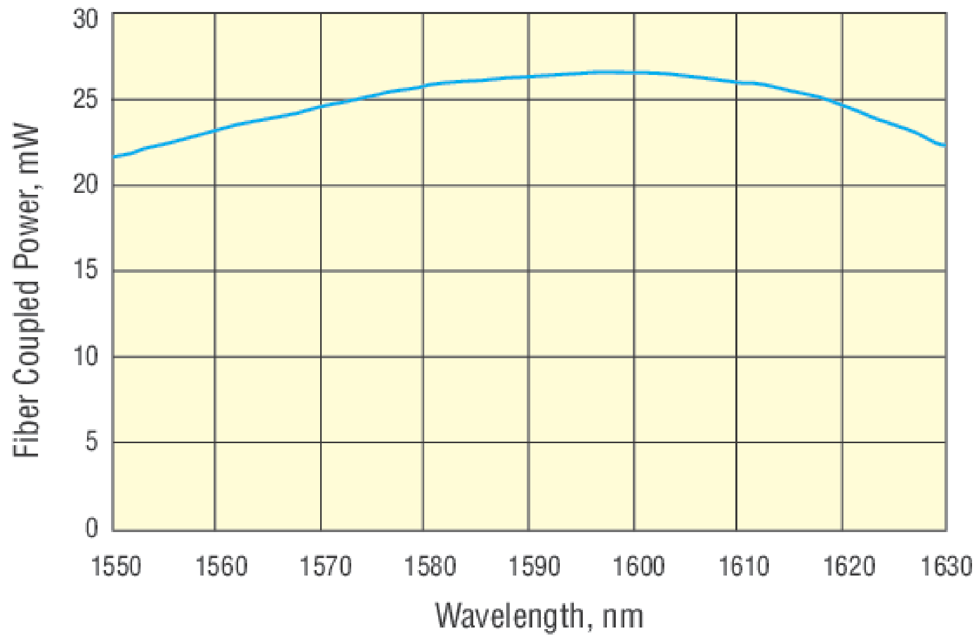
NIR lasers (MIRA 900)
Fs and CW modes
700-1050 nm

Vantage tunable diode

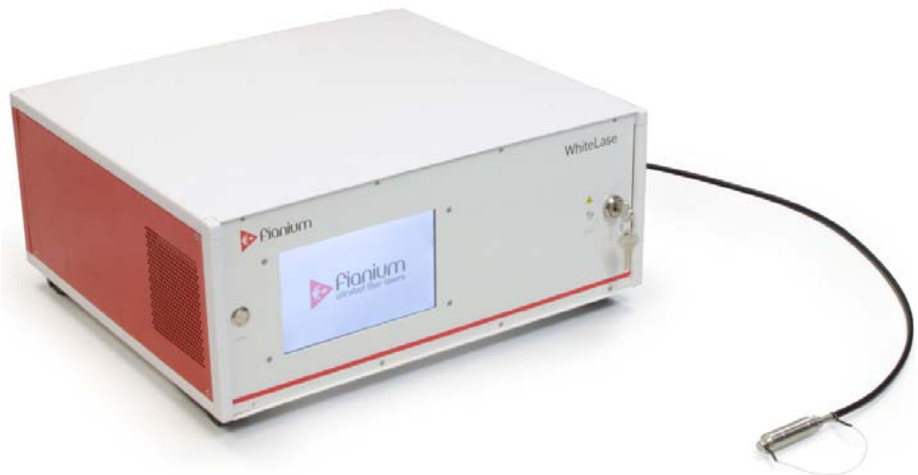


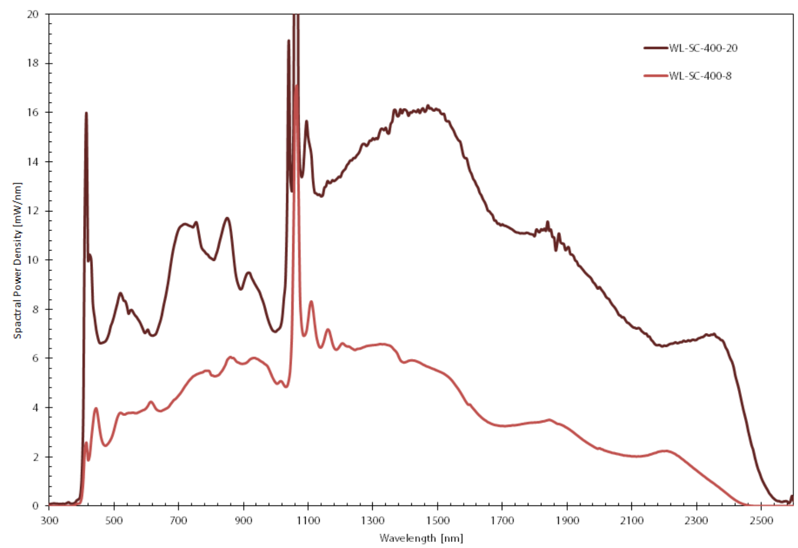
Tunable diodes

Spectra Physics Velocity™ Widely Tunable Lasers



Laser supercontinuum – good option for phototohermal spectroscopy





http://www.nktphotonics.com/